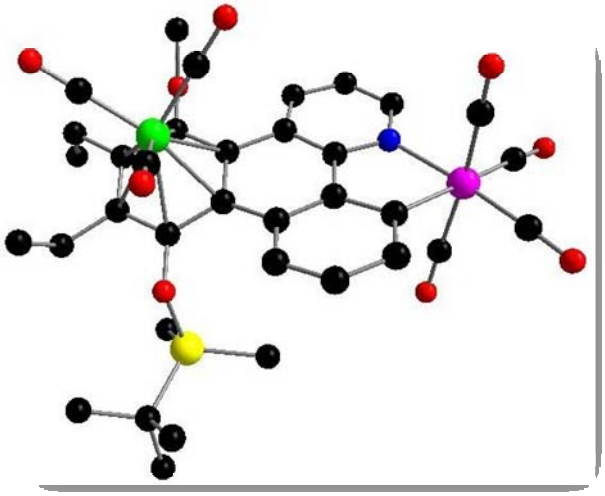
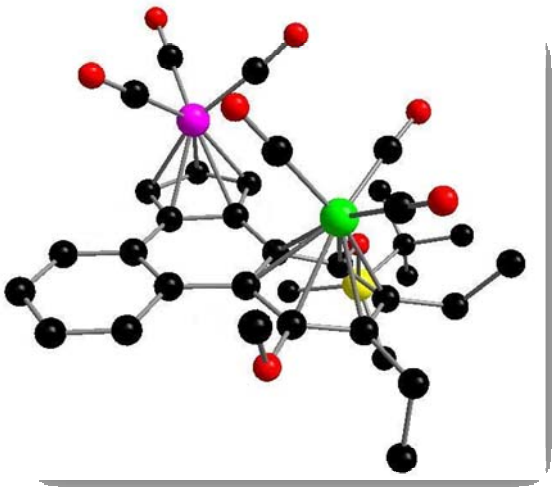
Novel Heterobimetallic Manganese-Chromium and Rhenium-Chromium Complexes: Coordination, Cyclometallation, Benzannulation and Haptotropic Metal Migration.





Dissertation zur Erlangung des Doktorgrades (Dr. rer. nat.) der Mathematisch-Naturwissenschaftlichen Fakultät der Rheinischen Friedrich-Wilhelms-Universität Bonn

Thèse de Doctorat en Chimie Moléculaire de l'Université Pierre et Marie Curie
Pour obtenir le grade de Docteur de l'Université Pierre et Marie Curie

vorgelegt von, présentée par

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« Dans la vie, il n'y a rien à craindre :
il n'y a que des choses à comprendre. »

Marie CURIE

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A ma bien-aimée Anna

Résumé en Français:

Une propriété caractéristique des complexes formés par des métaux de transition et des ligands polycycliques aromatiques est leur capacité à se soumettre à des réarrangements haptotropiques ; le fragment métallique est considéré comme le groupe fonctionnel déplaçable qui migre entre deux cycles non-équivalents du ligand hydrocarboné.

Nous avons décidé de coordiner d'autres métaux de transition aux complexes (polyarène)$Cr(CO)_3$ afin d'étudier leurs différentes influences sur la migration du tricarbonylchrome. Dans ce contexte, les premiers complexes hétérobimétalliques *syn* et *anti* $Cr(CO)_3$-$Mn(CO)_3$ et $Cr(CO)_3$-$Re(CO)_3$ ont été synthétisés. De plus, la synthèse de nouveaux complexes du tricarbonylchrome avec un polyarène *N*-hétérocyclique a été étudiée, ainsi que leur équivalents cyclomanganatés. Dans toutes ces synthèses, la benzannulation [3+2+1] de carbène de *Fischer* portant une unité métallique additionnelle a été employée afin d'introduire l'atome de chrome sur le ligand.

Les migrations haptotropiques thermiquement induites du chrome le long des plateformes aromatiques ont été exécutées sur tous les complexes et ont conduit dans la plupart des cas aux haptotropomères thermodynamiques souhaités. Les déplacements intramoléculaires du fragment chromique ont été confirmés avec des études cinétiques par RMN qui ont montré une cinétique de premier ordre. De plus, toutes les structures hétérobimétalliques ont été déterminées par des analyses cristallographiques.

Mots clés:

Chrome, Manganèse, Rhénium, Cyclomanganation, Carbène de Fischer, Benzannulation et Migration Haptotropique.

Résumé in English:

A characteristic property of transition metal π-complexes with polycyclic aromatic ligands is their ability to undergo haptotropic rearrangements; the metal fragment is considered as the moveable functional group that is shifted between two non-equivalent rings of an oligocyclic ligand.

We decided to add second different metal units coordinated to the (polyarene)$Cr(CO)_3$ complexes in order to study their influences on the migration of the chromium moiety. In this context, we synthesized the first *syn* and *anti* heterobimetallic $Cr(CO)_3$-$Mn(CO)_3$ and $Cr(CO)_3$-$Re(CO)_3$ oligocyclic fused-arene complexes. Moreover, we investigated a novel synthesis of (*N*-heterocyclic polyarene)$Cr(CO)_3$ and cyclomanganated (*N*-heterocyclic polyarene)$Cr(CO)_3$ complexes. In all binuclear cases, the chromium-templated-[3+2+1] benzannulation of *Fischer* arylcarbenes bearing an additional metal label was employed to introduce the chromium moiety.

The thermo-induced haptotropic chromium migrations along the π-face of the platforms were performed with all these complexes and yielded in most case to the desired thermodynamic haptotropomers. The intramolecular courses of the chromium fragment were confirmed by NMR-studies which revealed first order kinetics. Besides, all the heterobimetallic structures were determined by X-ray analyses.

Keywords:

Chromium, Manganese, Rhenium, Cyclomanganation, Fischer carbene, Benzannulation and Haptotropic Migration.

THESIS PLAN

I] INTRODUCTION

An organometallic compound (or organo-inorganic, metallo-organic and metalorganic) is a molecule containing one or several bonds between metal and carbon atoms.[1] As an extension, compounds containing metal-element bonds of a largely covalent character are also considered as organometallic compounds. In addition to the traditional metals, lanthanides, actinides, and semimetals, elements such as boron, silicon, arsenic, and selenium are considered to form organometallic compounds. Organometallic chemistry is in fact at the frontier between inorganic chemistry and organic chemistry and even also biochemistry. In the latter, the specialized study of compounds such as chlorophyll or hemoglobin is known as bioinorganic chemistry.

The discovery of ferrocene[2] in 1951 and its structural elucidation by two separate research groups the following year (E. O. Fischer proposed a *"Double-cone structure"*, G. Wilkinson a *"Sandwich Structure"*) marked the birth of contemporary organometallic chemistry. This revolutionary advance in organometallic chemistry was recognized with a Nobel Prize in Chemistry in 1973. This discovery opened an active field in chemistry with the continuous development of new sandwich complexes or metallocenes, bent metallocenes, half sandwich complexes etc, which will be partially discussed in this thesis.

In the meantime, metal carbene chemistry started in 1964 with E. O. Fischer[3] and the synthesis of a carbene complex via a sequential addition of a nucleophile and an electrophile. The discovery of a nucleophilic metal carbene by R. R. Schrock[4] in 1974 extended the topic.[5]

In 1975, K. H. Dötz[6] reported the chromium-templated-[3+2+1] benzannulation of α,β-unsaturated Fischer carbene complexes with alkynes to provide densely substituted benzenoid compounds with its *in-situ* complexation by a $Cr(CO)_3$ fragment, which will be intensively detailed in this work.

To conclude, Y. Chauvin,[7] R. R. Schrock[8] and R. H. Grubbs,[9] shared the Nobel Prize in Chemistry in 2005 for their work on metal-catalyzed olefin metathesis. Y. Chauvin proposed a non-pairwise alkylidene exchange mechanism; R. R. Schrock designed low-coordinated carbene complexes of molybdenum and tungsten; R. H. Grubbs developed ruthenium carbene catalysts for the ring-closure metathesis.[10]

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[4] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796.

[5] Special issue on Transition Metals Complexes of Carbenes and Related Species in 2000, *Journal of Organometallic Chemistry*, **2001**, Issue 1, Vol. 617-618.

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[7] Y. Chauvin, Olefin metathesis: the early days (Nobel lecture) *Angew. Chem. Int. Ed.* **2002**, *45(23)*, 3741.

[8] R. R. Schrock, Multiple metal-carbon bonds for catalytic metathesis reactions (Nobel lecture) *Angew. Chem. Int. Ed.* **2002**, *45(23)*, 3748.

[9] R. H. Grubbs, Olefin-metathesis catalysts for the preparation of molecules and materials (Nobel lecture) *Angew. Chem. Int. Ed.* **2002**, *45(23)*, 3760.

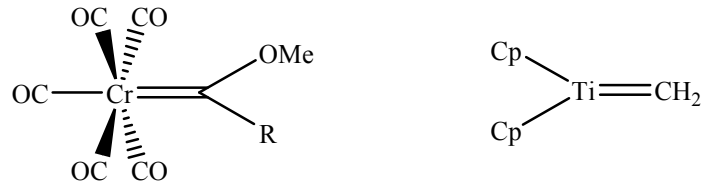
[10] Didier Astruc, *Organometallic Chemistry and Catalysis.* Berlin: Springer; **2007**.

II] BACKGROUND

1. Fischer carbene

1.1 Classification of metal carbene complexes

For a few decades metal carbenes have been mainly classified as Fischer or Schrock carbenes (**Figure 1**); this description is based on the different oxidation state of the metal center, a difference which results in different properties and consequently a different reactivity.
Metal carbenes are molecules with a neutral dicoordinate carbon atom linked to a metal center. They were introduced for the first time by Fischer and Maasböl in 1964[11] and Schrock expanded on this research 10 years later.[12]
Fischer-type carbene complexes[13] are electrophilic heteroatom-stabilized carbenes with metals in low oxidation states. The low-valent transition metal (Cr, Mo, W…) is usually stabilized by π-acceptor substituents (CO, PR_3, NO…).
Schrock-type carbene complexes[14] are nucleophilic alkylidene complexes formed by coordination of strong donor ligands such as alkyl or cyclopentadienyl with no π-acceptor ligands to metals (Mo, Ti, Ta, W…) in high oxidation states.



Fischer carbene complexes = good σ-acceptor, bad π-donor

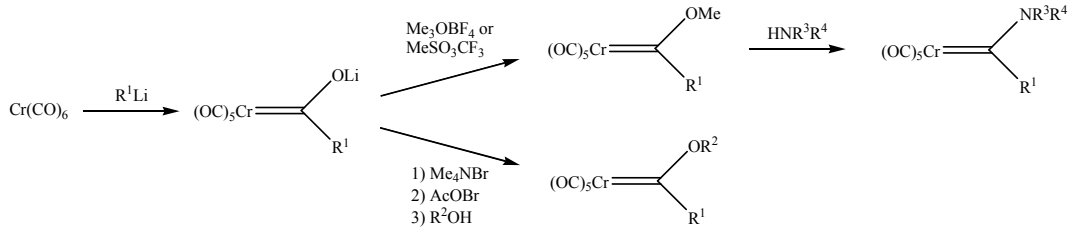
Schrock carbene complexes = good σ-acceptor, good π-donor

Figure 1: Fischer and Schrock carbene complexes

[11] E. O. Fischer, A. Maasböl, *Angew. Chem.* **1964**, *76*, 644.
[12] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796.
[13] (a) E. O. Fischer, *Angew. Chem.* **1974**, *86*, 651; (b) K. H. Dötz, H. Fischer, P. Hoffmann, F. R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, **1983**; (c) K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573; (d) W. D. Wulff, In *Comprehensive Organometallic Chemistry*; B. M. Trost, I. Flemming, Eds.; Pergamon Press: Oxford, **1991**; *Vol. 5*, p 1065; (e) W. D. Wulff, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, pp 469-547; (f) L. S. Hegedus, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, p 549; (g) G. Bertrand, "Transition Metal Complexes of Carbenes and Related Species in 2000", *J. Organomet. Chem.* **2001**, *617-618*, Special issue, 771 pages; (h) K. H. Dötz, H. C. Jahr, In *Carbene Chemistry – From fleeting intermediates to powerful reagents*, G. Bertrand (Ed.), FontisMedia, Lausanne, Marcel Dekker, New York, **2002**, *231*; (i) J. Barluenga, J. Santamaria, M. Thomas, *Chem. Rev*., **2004**, 2259; (j) K. H. Dötz, A. Koch, M. Wermer, In P. Knochel (Ed.) *Handbook of Functionalized Organometallics – Applications in Synthesis*, Wiley-VCH Verlag, **2005**, 451.
[14] (a) R. R. Schrock, *Acc. Chem. Res.* **1979**, *12*, 98; (b) A. Fürstner, *Alkene Metathesis in Organic Synthesis, Top. Organomet. Chem.*, Springer Verlag, Berlin Heidelberg, **1998**; (c) R. H. Grubbs, (Ed.) *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**; (d) S. J. Connon, S. Blechert, *Ruthenium Catalysts and Fine Chemistry*, *Top. Organomet. Chem.*, **2004**; (e) B. Schmidt, J. Hermanns, In K. H. Dötz (Ed.) *Metal Carbenes in Organic Synthesis*, *Top. Organomet. Chem.*, 13, 223, Springer Verlag, Berlin Heidelberg, **2004**.

1.2 Synthesis of Fischer carbene complexes

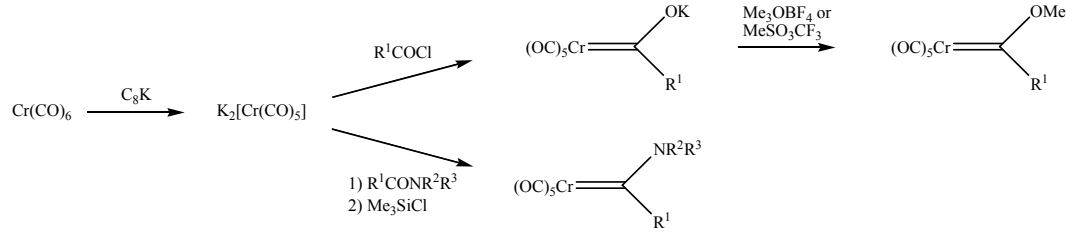
Fischer carbene complexes can be prepared by two established syntheses. In the Fischer route (**Scheme 1**),[15] the one originally reported by Fischer, they are prepared from $M(CO)_6$ (M= Cr, W, Mo) by reaction of an organolithium compound with one of the carbonyl ligands to form an anionic lithium acylmetallate which is followed by an *O*-alkylation with Meerwein salt[16] $[Me_3O][BF_4]$ or methylester-trifluoromethansulfonic acid (methyltriflat).



Scheme 1: So-called *Fischer* route for the synthesis of carbene complexes

However, in this case the alkylation leads only to methoxy- or ethoxy-substituted Fischer carbene complexes. In order to extend the variety of the alkoxycarbene complexes, it is possible to make the acylmetallate react with tetramethylammonium salt and then acetyl bromide to form a highly reactive acyloxycarbene complex which will be then alcoholised. The aminolysis of the methoxycarbene complex, i.e. replacing the alkoxy group by amines via an addition-elimination mechanism, leads to the equivalent aminocarbene complexes.

In the second synthesis, the Semmelhack-Hegedus route,[17] the chromium hexacarbonyl is reduced with C_8K, elementary potassium or potassium naphthalide to dipotassium chromate (II) intermediate, which then reacts with an acid chloride to give the acylchromate. Finally, the acylchromate is *O*-alkylated with a Meerwein salt to yield the Fischer carbene complex.[18] The aminocarbene complexes are also attainable in this synthesis, by reaction of the chromate with an amide; the use of the oxophile trimethylsilylchloride is necessary to achieve the reaction (**Scheme 2**).[19]



Scheme 2: *Semmelhack Hegedus* route for the synthesis of carbene complexes

[15] (a) E. O. Fischer, A. Maasböl, *Chem. Ber.* **1967**, *100*, 2445; (b) R. Aumann, E. O. Fischer, *Angew. Chem.* **1967**, *79*, 900.
[16] H. Meerwein, G. Hinz, P. Hoffmann, E. Kroning, *J. Prakt. Chem.* **1937**, *147*, 257.
[17] (a) K. Öfele, *Angew. Chem.* **1968**, *80*, 1032; (b) C. W. Rees, E. von Angerer, *J. Chem. Soc., Chem. Comm.* **1972**, 420; (c) M. F. Semmelhack, G. R. Lee, *Organometallics*, **1987**, *6*, 1839; (d) R. Imwinkelried, L. S. Hegedus, *Organometallics*, **1988**, *7*, 702; (e) M. A. Schwindt, J. R. Miller, L. S. Hegedus, *J. Organomet. Chem.* **1991**, *413*, 143.
[18] K. H. Dötz, W. Straub, R. Ehlenz, R. Meisel, K. Peseke, *Angew. Chem.* **1995**, *107*, 2023.
[19] K. H. Dötz, W. C. Haase, M. Klumpe, M. Nieger, *Chem. Comm.*, **1997**, 1217.

1.3 Reactivity of Fischer carbene complexes

Fischer carbene complexes are strongly electrophilic and can consequently easily be attacked by nucleophiles such as amines. This reactivity can be understood as an electron-deficient carbene carbon atom due to the electron-withdrawing character of the CO groups, while the alkoxy group stabilizes the carbene. Likewise the α proton has an enhanced acidity which allows its deprotonation and the modification of the side chain by reaction with an electrophile. Electrophiles can also react with the heteroatoms of the alkoxy- or aminocarbene complexes. Finally, the carbonyl groups in the coligand sphere can be exchanged with other ligands such as phosphines (**Figure 2**).[20]

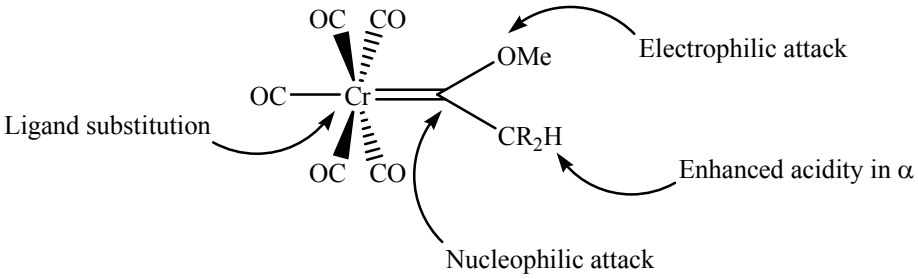


Figure 2: Fischer carbene complex reactivity

1.4 Reactions of Fischer carbene complexes

By referring to the reactivity of Fischer carbene complexes, different kinds of reaction are possible (**Figure 3**). By working on the acidity of the α proton, it is possible to cause α-alkylation[21] and aldolisation.[22] With an α,β-unsaturated Fischer carbene complex, regioselective *Michael* additions are possible,[23] as are *Diels-Alder* reactions.[24] The chromium-templated-[3+2+1] benzannulation reaction is explained in detail in the next chapter (**I] 2. Benzannulation**).

[20] (a) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, H. Lorenz, *Angew. Chem.* **1973**, *85*, 618; (b) H. Fisher, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert, K. Weis, *Carbyne Complexes*, VCH-Verlag, Weinheim, **1988**; (c) E. Riedel, C. Janiak, T. M. Klapötke, H.-J. Meyer, *Moderne Anorganische Chemie*, Walter de Gruyter, Berlin, New York, **1999**, p. 628.

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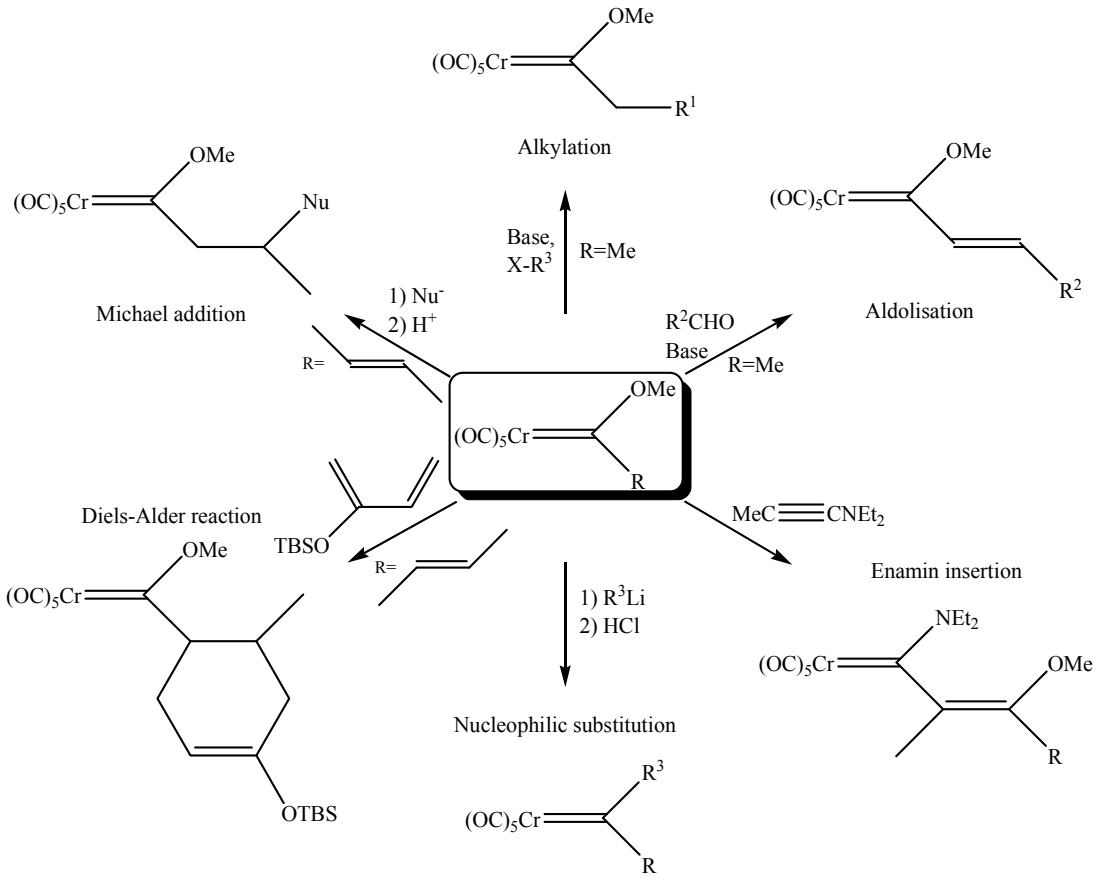


Figure 3: Fischer carbene complex synthetic potential

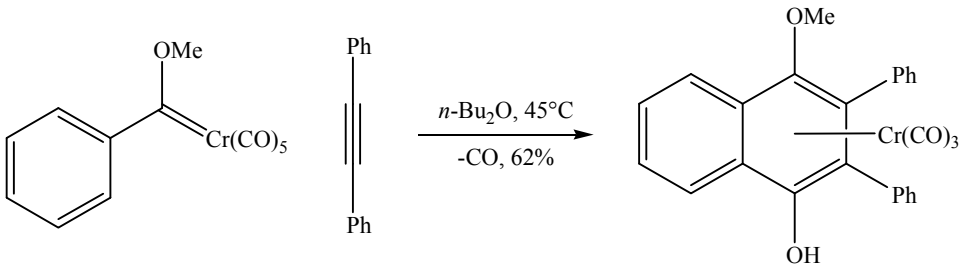
2. Benzannulation

2.1 Benzannulation reaction

The chromium-templated-[3+2+1] benzannulation reaction of α,β-unsaturated Fischer carbene complexes with alkynes was reported for the first time in 1975 by K. H. Dötz[25] (**Scheme 3**). Since then, further research on this reaction has resulted in the development of a unique organometallic template in the stereocontrol of a one-pot formation of densely substituted benzenoid compounds with its *in-situ* complexation by a $Cr(CO)_3$-fragment.[26]

[25] K. H. Dötz, *Angew. Chem.* **1975**, *87*, 672.

[26] (a) K. H. Dötz, *Angew. Chem. Int. Ed. Engl.*, **1984**, *23*, 587; *Angew. Chem.*, **1984**, *96*, 573; (b) M. F. Semmelhack, *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, Chapter 9, p 979; (c) W. D. Wulff, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, pp 469-547; (d) M. J. Morris, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; J. A. Labinger, M. J. Winter, Vol. Eds.; Pergamon: Oxford, UK, **1995**; *Vol. 5*, pp 501-504; (e) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.*, **1999**, *28*, 187; (f) K. H. Dötz, J. Stendel Jr., In *Modern Arene Chemistry*; D. Astruc, Ed.; Wiley-VCH: Weinheim, 2002; pp 250-296; (g) K. H. Dötz, H. C. Jahr, *Chem. Rec.* **2004**, *4*, 61. (j) A. Minatti, K. H. Dötz, *Top. Organomet. Chem.*, **2004**, *13*, 123; (h) Dötz, K. H.; Wenzel, B.; Jahr, H. C. *Top. Curr. Chem.* **2004**, *248*, 63-103.



Scheme 3: The chromium-mediated benzannulation reaction

The [3+2+1]-cycloaddition takes place in ethereal solvents (*n*-Bu_2O, *tert*-butyl methyl ether…) upon gentle warming (around 50°C). This stepwise reaction involves an α,β-unsaturated carbene ligand as the C_3-synthon, an alkyne as the C_2-synthon, and a carbonyl ligand as the C_1-synthon, all arranged by the coordination sphere of the chromium-template, in an octahedral configuration (**Figure 4**). Actually, different functional groups within both the carbene complex and the alkyne can be used to yield a large range of densely substituted phenols.[27]

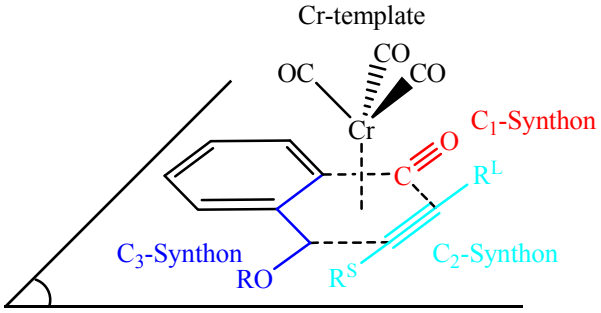


Figure 4: The chromium-templated-[3+2+1] benzannulation

2.2 Mechanism

The first step of the benzannulation involves, upon gentle warming, the reversible loss of a carbonyl ligand from the pentacarbonylaryl(alkoxy)carbene **A** to yield the coordinatively unsaturated tetracarbonylcarbene complex **B**. In the subsequent step, this 16-electron complex coordinates to the alkyne present in the solution to give an 18-electron saturated carbene complex **C**. In the next step the alkyne ligand inserts itself into the metal-carbene bond to afford a (η^1:η^3)-vinylcarbene complex **D**. Then this (η^1:η^3)-vinylcarbene complex in (*E*)-configuration (required for the benzannulation) changes into an η^4-vinylketene complex **E** following the carbonyl ligand insertion into the chromium-carbene bond. This is followed by an electrocyclic ring closure to give a η^4-cyclohexadienone-chromium complex **F**. Finally, the keto-enol tautomerisation of this cyclohexadienone leads to the desired hydroxyarene-tricarbonylchromium complex **G** (**Scheme 4**).[28]

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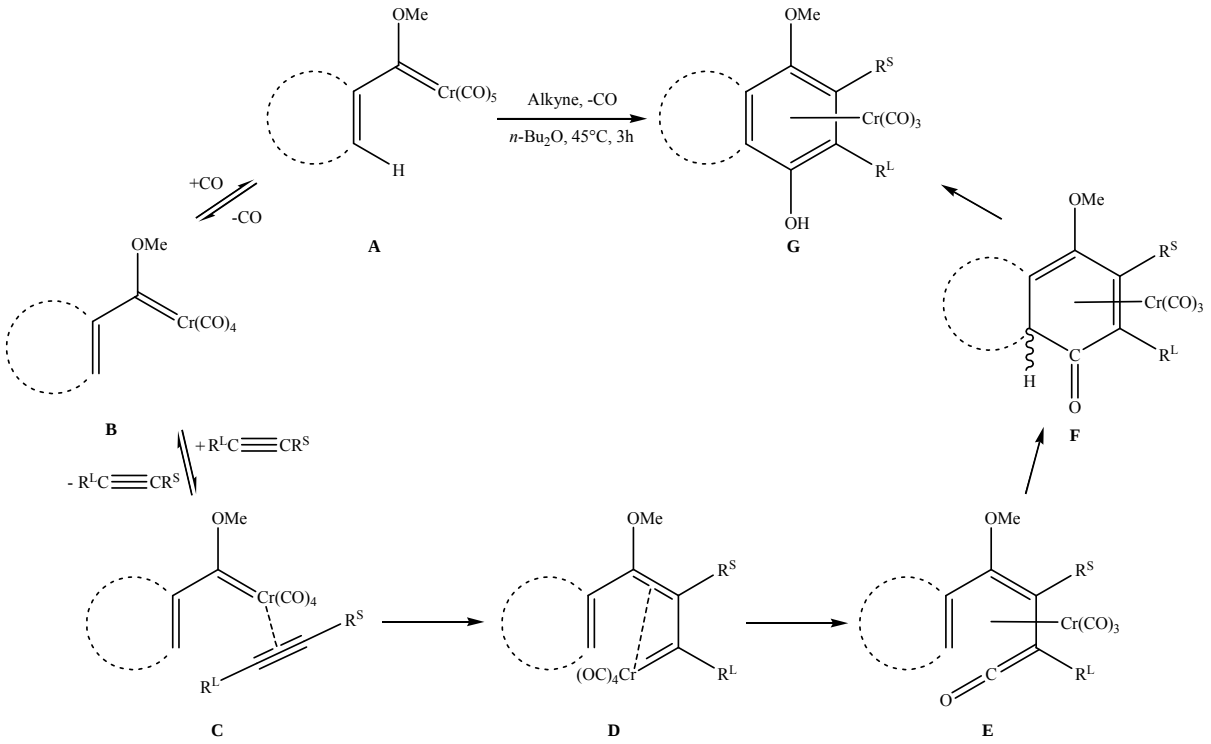
[27] (a) K. H. Dötz, D. B. Grotjahn, K. Harms, *Angew. Chem.*, **1989**, *101*, 1425; (b) B. A. Anderson, W. D. Wulff, T. S. Powers, S. Tribbitt, A. L. Rheingold, *J. Am. Chem. Soc.* **1992,** *11***,** 10784.

[28] (a) K. H. Dötz, B. Fügen-Köster, *Chem. Ber.*, **1980**, *113*, 1449; (b) K. H. Dötz, J. Mühlemeier, *Angew. Chem.*, **1982**, *94*, 2023; (c) M. Gleichmann, B. A. Hess, K. H. Dötz, *J. Am. Chem. Soc.*, **1986**, *118*, 10551; (d) P. Hofmann, M. Hämmerle, *Angew. Chem.*, **1989**, *101*, 940; (e) B. A. Anderson, W. D. Wulff, A. L. Rheingold, *J. Am. Chem. Soc.* **1990,** *112***,** 8615; (f) E. Chelain, A. Parlier, H. Rudler, J. C. Daran, J. Vaissermann, *J. Organomet. Chem.* **1991**, *419*, C5; (g) P. Hofmann, M. Hämmerle,G. Unfried, *New J. Chem.*, **1991**, *15*, 769; (h)



Scheme 4: Benzannulation – Suggested mechanism

2.3 Chemo-, regio-, stereoselectivity and annulation pattern

The chemoselectivity of the benzannulation of α,β-unsaturated Fischer carbene complexes is greatly favoured in the formation of phenol. Nevertheless, by-products such as indene or furan derivates are known to arise from a (*Z*)-configuration of the (η^1:η^3)-vinylcarbene complex (**Scheme 5**). These by-products can even become major products under special conditions; a strongly polar or strongly coordinating solvent,[29] the concentration of the alkyne[30] or the nature of the metal[31] can play an important role in the ratio of [3+2+1]-benzannulation to [3+2]-cyclopentaannulation. In the case of aminocarbene complexes, cyclopentannulated compounds are also preferred.[32]

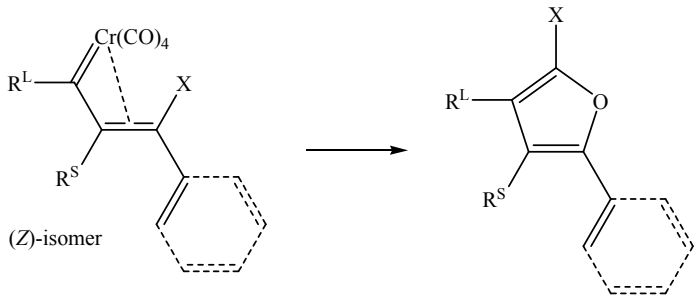
K. H. Dötz, T. Schäfer, F. Kroll, K. Harms, *Angew. Chem.*, **1992**, *104*, 1257; (i) W. D. Wulff, B. M. Bax, T. A. Branvold, K. S. Chan, A. M. Gilbert, R. P. Hsung, J. Mitchell, J. Clardy, *Organometallics*, **1994**, *13*, 102; (j) J. Barluenga, F. Aznar, A. Martin, M. S. Garcia-Granda, E. J. Perez-Carreno, *J. Am. Chem. Soc.*, **1994**, *116*, 11191; (k) M. Torrent, M. Duran, M. Sola, *J. Am. Chem. Soc.*, **1999**, *121*, 1309.

[29] K. S. Chan, G. A. Peterson, T. A. Brandvold, K. L. Faron, C. A. Challener, C. Heydahl, W. D. Wulff, *J. Organomet. Chem.* **1987**, *334*, 9.

[30] M. E. Bos, W. D. Wulff, R. A. Chamberlin, T. A. Brandvold, *J. Am. Chem. Soc.* **1991,** *113***,** 9293.

[31] (a) N. H. T. Huy, P. Lefloch, *J. Organomet. Chem.* **1988**, *344*, 303; (b) T. A. Brandvold, W. D. Wulff, A. D. Rheingold, *J. Am. Chem. Soc.*, **1990**, *112*, 1645; (c) K. H. Dötz, H. Larbig, *J. Organomet. Chem.* **1991**, *405*, 38; (c) D. F. Harvey, E. M. Grenzer, *J. Am. Chem. Soc.*, **1994**, *116*, 6719.

[32] (a) A. Yamashita, *Tetrahedron Lett.* **1986**, *27*, 5915; (b) D. B. Grotjahn, K. H. Dötz, *Synlett*, **1991**, 381



Scheme 5: Formation of furan products

The benzannulation is regioselective with the use of unsymmetrical alkynes; indeed, the major regioisomer generally bears the smallest alkyne subsistent in *ortho* position of the alkoxy function because of steric reasons during the alkyne's insertion into the chromium-carbene bond.[33] A reversal regioselectivity is possible to achieve by the use of stannyl-,[34] silyl- acetylenes,[35] alkynyl boronates[36] and by an intramolecular reaction where the alkyne is incorporated into the alkoxy chain (**Figure 5**).[37]

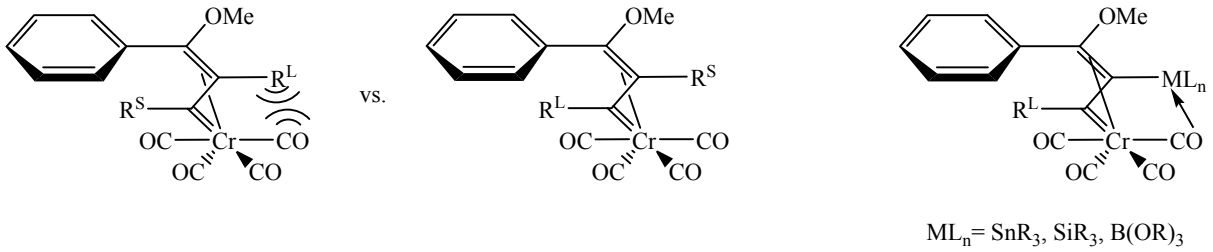
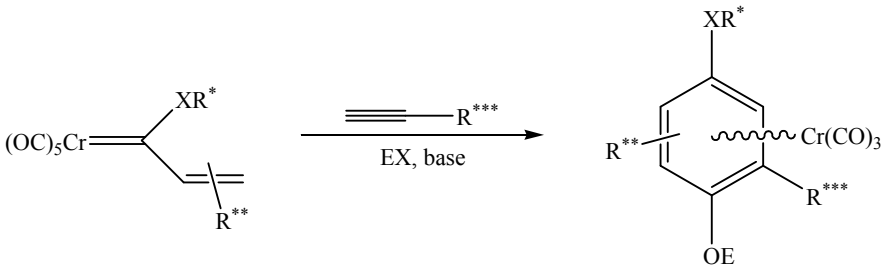


Figure 5: Regioselectivity of alkyne insertion and inverse regioselectivity

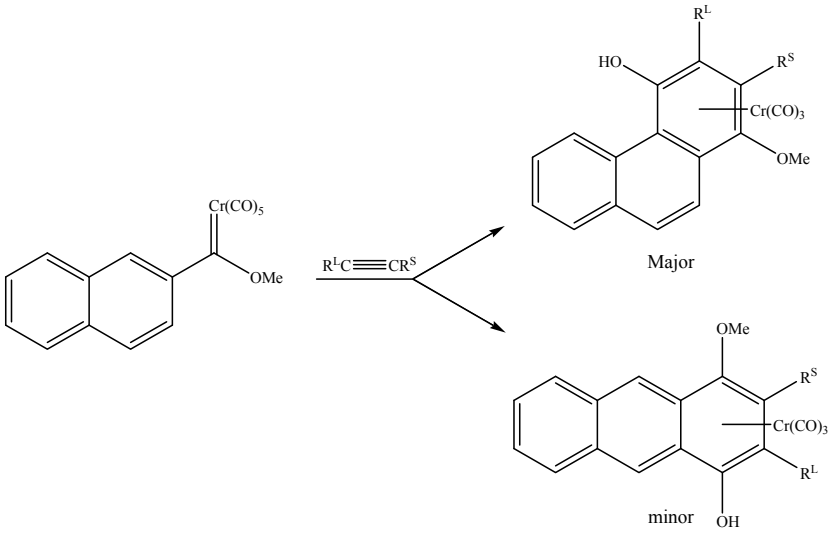
Due to the intrinsic asymmetric arene substitution pattern, the benzannulation reaction leads under achiral conditions to a racemic mixture of enantiomeric tricarbonylchromium complexes with a planar chirality. In order to form enantiopure as well as diastereopure compounds, the introduction of a stereogenic element is necessary. This can be done at three different points: in the alkyne side chain,[38] in the carbene carbon side chain[39] or in the alkoxy- or amino-carbene side chain (**Scheme 6**).[40]

[33] K. H. Dötz, R. Dietz, A. von Imhoff, H. Lorenz, G. Huttner, *Chem. Ber.*, **1976**, *109*, 2033.
[34] S. Chamberlain, M. L. Waters, W. D. Wulff, *J. Am. Chem. Soc.*, **1994**, *116*, 3113.
[35] J. C. Anderson, R. M. Denton, H. G. Hickin, C. Wilson, *Tetrahedron*, **2004**, *60*, 2327.
[36] M. W. Davies, C. N. Johnson, J. P. A. Harrity, *J. Org. Chem.* **2001**, *66*, 3525.
[37] M. F. Gross, M. G. Finn, *J. Am. Chem. Soc.*, **1994**, *116*, 10921.
[38] (a) R. P. Hsung, W. D. Wulff, *J. Am. Chem. Soc.*, **1994**, *116*, 6449; (b) R. P. Hsung, J. F. Quinn, B. A. Weisenberg, W. D. Wulff, G. P. A. Yap, A. L. Rheingold, *Chem. Comm.* **1997**, 615; (c) S. R. Pulley, J. P. Carey, *J. Org. Chem.* **1998**, *63*, 5275; (d) D. Paetsch, K. H. Dötz, *Tetrahedron Lett.* **1999**, *40*, 487; (e) O. Kretschnik, M. Nieger, K. H. Dötz, *Organometallics*, **1996**, *15*, 3625
[39] (a) R. P. Hsung, W. D. Wulff, C. A. Challener *Synthesis*, **1996**, 773; (b) J. D. King, P. Quayle, *Tetrahedron Lett.* **1991**, *32*, 7759; (c) R. L. Beddoes, J. D. King, P. Quayle, *Tetrahedron Lett.* **1995**, *36*, 3027.
[40] (a) K. H. Dötz, C. Stinner, M. Nieger, *J. Chem. Soc. Chem. Comm.* **1995**, 2535; (b) K. H. Dötz, C. Stinner, *Tetrahedron: Asymmetry* **1997**, *8*, 1751.



Scheme 6: Pathways to a diastereoselective benzannulation

The benzannulation of *ortho*-unsubstituted polycyclic arene Fischer carbene complexes can *a priori* lead to a competition between linear and angular annulation products, but generally the reactions' products of the 2-naphthyl carbene complexes and their homologues with alkynes are strongly favourable over the angular phenanthrene benzannulation compound (**Scheme 7**).[41] This regioselectivity can be explained by the significant difference in their relative energies (by ca. 25 kJ.mol^{-1} for the parent compounds) in favour of the angular product. Only one case has been reported where the linear anthracene benzannulation product is favoured[42] and it has also been demonstrated that the benzannulation of dibenzofuran and -thiophene carbene complex can afford the two regioisomers nearly in equal amounts.[43]



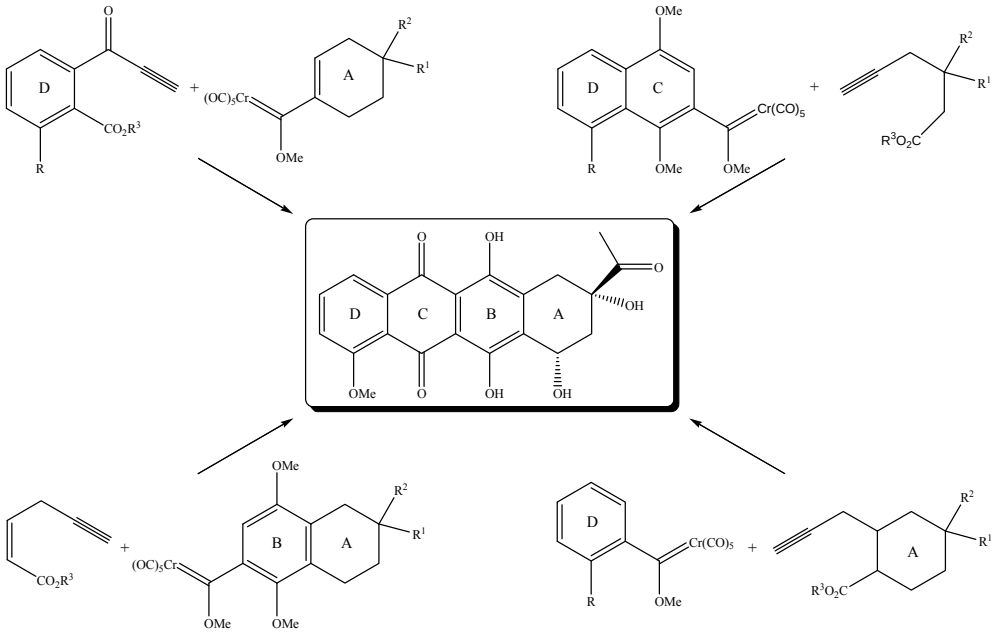
Scheme 7: Annulation pattern

2.4 Examples of application: total synthesis.

Four different strategies, all involving the [3+2+1] benzannulation as a key step reaction, are conceivable to build the tetracyclic daunomycinone.[44] This member of the antitumour

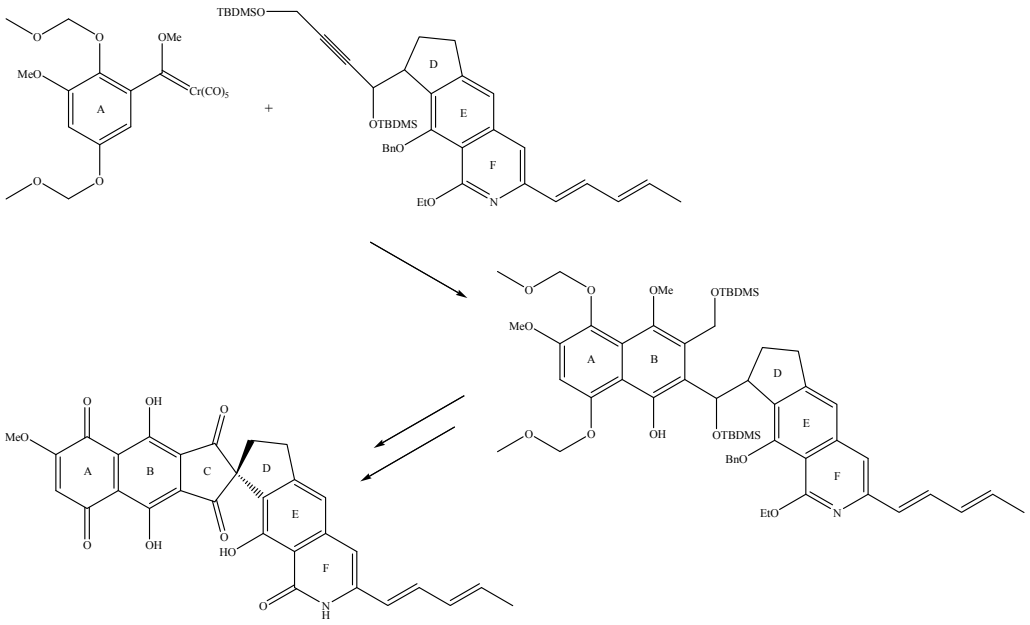
[41] M. F. Semmelhack, S. Ho, D. Cohen, M. Steigerwald, M. C. Lee, G. Lee, A. M. Gilbert, W. D. Wulff, R. G. Ball, *J. Am. Chem. Soc.*, **1994**, *116*, 7108.
[42] K. H. Dötz, M. Popall, *J. Organomet. Chem.*, **1985**, *C1*, 295.
[43] (a) H. C. Jahr, M. Nieger, K. H. Dötz, *J. Organomet. Chem.*, **2002**, *641*, 185; (b) K. H. Dötz, H. C. Jahr, *Chem. Rec.* **2004**, *4*, 61. (j) A. Minatti, K. H. Dötz, *Top. Organomet. Chem.*, **2004**, *13*, 123.
[44] (a) W. D. Wulff, P. C. Tang, *J. Am. Chem. Soc.*, **1984**, *106*, 434; (b) W. D. Wulff, P. C. Tang, K. S. Chan, J. S. McCallum, D. C. Yang, S. R. Gilbertson, *Tetrahedron* **1985**, *41*, 5813; (c) K. H. Dötz, M. Popall, *Angew. Chem. Int. Ed. Engl.*, **1987**, *99*, 1158; (d) W. D. Wulff, Y. C. Xu, *J. Am. Chem. Soc.*, **1988**, *110*, 2312.

antibiotics anthracycline family contains a quinone C ring and a juxtaposed hydroquinone B ring and both of these two rings can be constructed by the benzannulation reaction (**Scheme 8**).



Scheme 8: Carbene complex strategies to daunomycinone.

The synthesis of the antitumoral antibiotic fredericamycin A[45] also needs, among other reaction steps, a regiospecific intermolecular [3+2+1] benzannulation as a key step reaction to build the polycyclic core of the molecule (**Scheme 9**).



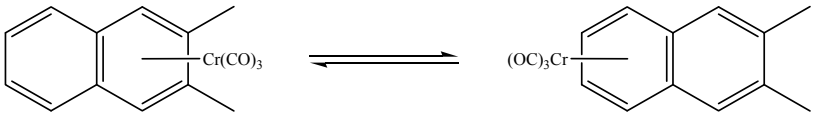
Scheme 9: Total synthesis of the antitumoral agent Fredericamycin A

[45] D. L. Boger, I. C. Jacobsen, *J. Am. Chem. Soc.*, **1995**, *117*, 11839.

3. Haptotropic metal migration along arene platforms

3.1 Thermal-induced haptotropic migration

Haptotropic metal migration occurs with transition metal π-complexes, in which the π-bound ligand offers different coordination sites.[46] The metal fragment can be considered as the moveable functional group that is shifted between two non-equivalent rings of a fused-arene ligand. These η^6-η^6 metal shifts have already been widely studied with naphthalene[47], phenanthrene[48] and tetracyclic fused-arene[49] tricarbonylchromium complexes, in which extended aromatic ligands with heteroarene spacers were chosen to evaluate their compatibility with the haptotropic metal migration.
The first π,π-rearrangement of a tricarbonylchromium on naphthalene derivatives was discovered by Deubzer and Öfele in 1967 (**Scheme 10**).[50] This reversible migration was proved by crystallisation of the products. The use of naphthalene would lead to a degenerated haptotropic rearrangement involving identical starting material and rearranged product.



Scheme 10: First haptotropic tricarbonylchromium rearrangement

In the eighties, Treichel and Kündig developed the study of the haptotropic migration by calculating the rate constants and thermodynamic activation parameters for mono- and polydeuterated π-complexes, demonstrating a first-order kinetic which implies an intramolecular process.[51] Further confirmation of an intramolecular shift of the metal moiety was provided by Oprunenko through the use of diastereomerically pure methylacenaphthalene complexes (**Scheme 11**).[52]

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[46] (a) K. H. Dötz, *Angew. Chem. Int. Ed. Engl.*, **1984**, *23*, 587; *Angew. Chem.*, **1984**, *96*, 573; (b) N. A. Ustynyuk, *Organomet. Chem. USSR* **1989**, *2*, 20-26; *Metalloorg. Khim.* **1989**, *2*, 43-53; *Chem. Abstr.* **1989**, *111*, 115236; (c) M. F. Semmelhack, *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, Chapter 9, p 979; (d) W. D. Wulff, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, pp 469-547; (e) M. J. Morris, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; J. A. Labinger, M. J. Winter, Vol. Eds.; Pergamon: Oxford, UK, **1995**; *Vol. 5*, pp 501-504; (f) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.*, **1999**, *28*, 187; (g) K. H. Dötz, J. Stendel Jr., In *Modern Arene Chemistry*; D. Astruc, Ed.; Wiley-VCH: Weinheim, 2002; pp250-296; (h) Y. F. Oprunenko, *Russ. Chem. Rev.* **2000**, *69*, 683-704; *Usp. Khim.* **2000**, *69*, 744-746; *Chem. Abstr.* **2000**, *134*, 178576; (i)K. H. Dötz, H. C. Jahr, *Chem. Rec.* **2004**, *4*, 61. (j) A. Minatti, K. H. Dötz, *Top. Organomet. Chem.*, **2004**, *13*, 123; (k) Dötz, K. H.; Wenzel, B.; Jahr, H. C. *Top. Curr. Chem.* **2004**, *248*, 63-103

[47] (a) K. H. Dötz, N. Szesni, M. Nieger, K. Nättinen, **2003**, *671*, 58; (b) K. H. Dötz, H. C. Jahr, *Chem. Rec.* **2004**, *4*, 61; (c) H. C. Jahr, M. Nieger, K. H. Dötz, *Chem.Eur. J.*, **2005**, *11*, 5333.

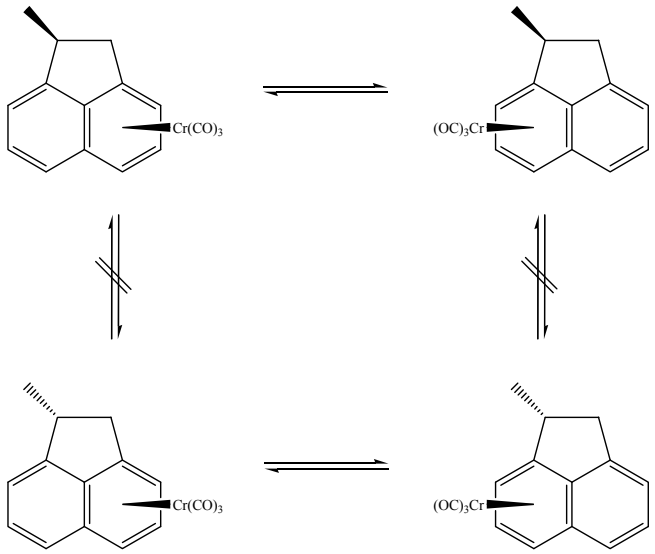
[48] K. H. Dötz, J. Stendel, Jr., S. Müller, M. Nieger, S. Ketrat, M. Dolg, *Organometallics*, **2005**, *24*, 3219.

[49] H. C. Jahr, M. Nieger, K. H. Dötz, *J. Organomet. Chem.*, **2002**, *641*, 185.

[50] B. Deubzer, H. P. Fritz, C. G. Kreiter, K. Öfele, *J. Organomet. Chem.*, **1967**, *7*, 289.

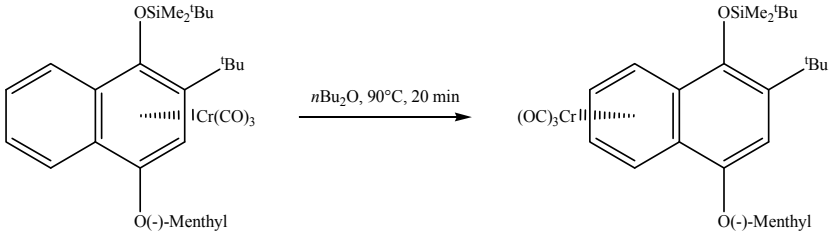
[51] (a) R. U. Kriss, P. M. Treichel, *J. Am. Chem. Soc.*, **1986**, *108*, 853; (b) E. P. Kündig, V. Desobry, C. Rivet, B. Rudolph, S. Splicher, *Organometallics*, **1987**, *6*, 1173.

[52] Y. F. Oprunenko, S.G. Malyugina, O. I. Trifonova, O. Y. Babushkina, A. P. Pisarevskii, Y. A. Ustynyuk, N. A. Ustynyuk, D. N. Krastov, P. N. Nesterenko, *Bull. Acad. Sci. USSR, Chem. Sci.* **1988**, 357.



Scheme 11: Haptotropic migration on methylacenaphtalene complexes

In 1997, Dötz described a diastereoselective chromium-templated [3+2+1]-benzannulation by introducing a chiral agent into the alkoxy-carbene side chain.[53] This (-)-menthyloxy-substituted naphthalene complex led to the best proof that the haptotropic migration's mechanism was intramolecular, the metal fragment moving from the kinetic ring to the thermodynamic one but staying on the same face of the naphthalene ligand (**Scheme 12**).

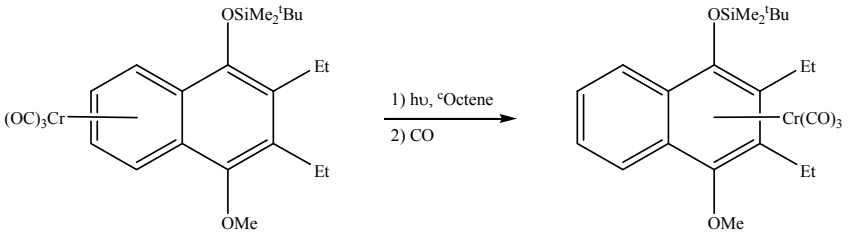


Scheme 12: Haptotropic metal migration

3.2 Coligand-induced reverse migration

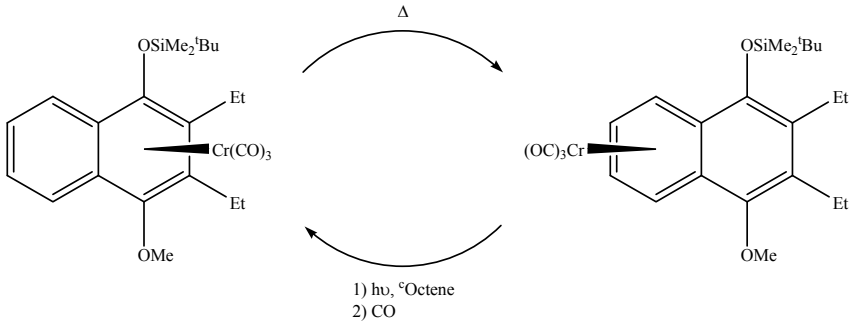
In 2004, Dötz et al. carried out further research into the metal moiety's reverse migration to the thermodynamically less-favoured isomer.[54] By tuning the coligand sphere of the chromium fragment, they noticed that the replacement of a CO ligand with a cyclooctene ligand was accompanied by a reverse metal shift. They tried to encourage this process and irradiated the tricarbonylchromium complex in order to decarbonylate one equivalent of carbon monoxide. Then the solution was flushed with a carbon monoxide flow instead of offering a phosphine donor ligand and followed by IR until the bands of the (cyclooctene)dicarbonylchromium complex disappeared (**Scheme 13**). The use of cyclooctene is necessary to trap the dicarbonylchromium species as a η^2-alkene complex in order to avoid decomplexation.

[53] K. H. Dötz, C. Stinner, *Tetrahedron: Asymmetry* **1997**, *8*, 1751.
[54] Dötz, K. H.; Wenzel, B.; Jahr, H. C. *Top. Curr. Chem.* **2004**, *248*, 63-103.



Scheme 13: Coligand-induced reverse metal shift

The experiment was then tested with enantiopure complexes and the chiral information was retained through the organometallic molecular switch (**Scheme 14**). Thus the first example of a racemization-free organometallic switch was elaborated.



Scheme 14: Stereospecific organometallic molecular switch

4. Synthesis of arene-tricarbonyl metal complexes

4.1 Chromium complexes

The complexation of an arene with a tricarbonylchromium moiety was first described in 1957 by E. O. Fischer and K. Öfele with the synthesis of a benzene tricarbonylchromium complex.[55] Arene tricarbonylchromium complexes are generally prepared from the thermolysis of $Cr(CO)_6$ under an inert atmosphere in the presence of an excess of the arene. Most of the time, the reaction takes place in a mixture of absolute dibutylether/tetrahydrofuran (9:1) at reflux, usually between one and four days long. Milder complexation conditions are possible with the use of $Cr(CO)_3L_3$ where L = MeCN, NH_3 and pyridine[56] or a ligand exchange with naphthalene$Cr(CO)_3$[57] and finally, the chromium-templated-[3+2+1] benzannulation described previously which is a very good alternative for the synthesis of poly-substituted polyarene tricarbonylchromium complexes.
The coordination of a tricarbonylchromium on an arene ligand modifies dramatically the reactivity of the arene ligand in several ways; one strong effect is the acidification of the ring protons and the protons in α-position of the ring which allows direct proton abstraction trapped then with electrophiles to provide substituted arene complexes (**Figure 6**).[58]

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[55] E. O. Fischer, K. Öfele, *Chem. Ber.*, **1957**, *90*, 2532.
[56] K. Öfele, *Chem. Ber.*, **1966**, *99*, 1752.
[57] E. P. Kündig, C. Perret, S. Spichiger, G. Bernardelli, *J. Organomet. Chem.*, **1985**, *286*, 183.
[58] (a) K. H. Dötz, *Angew. Chem. Int. Ed. Engl.*, **1984**, *23*, 587; *Angew. Chem.*, **1984**, *96*, 573; (b) M. F. Semmelhack, *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, Chapter 9, p 979; (c) W. D. Wulff, In *Comprehensive*

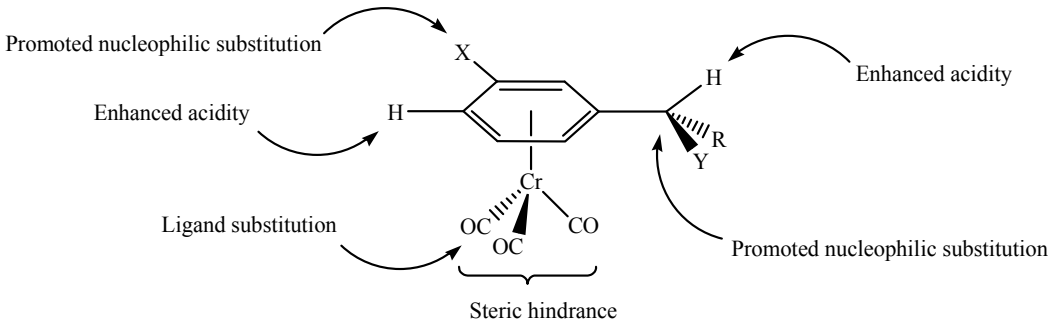

Figure 6: Synthetic potential of the arene tricarbonylchromium complexes

4.2 Manganese complexes

The tricarbonylmanganese entity is known to have two forms of complexation with cycloconjugated π-systems: the cationic (η^6-arene)$Mn(CO)_3$ complexes[59] and the neutral (η^5-Cp-ligand)$Mn(CO)_3$ complexes.[60] Our interest will focus on the latter. In 1970, Efraty and King described the syntheses of these compounds in the case of the indene and fluorene ligands, via the use of 50% sodium dispersion in mineral oil boiled under reflux of tetrahydrofuran to produce the corresponding complexes respectively in 56% and 11% yields.[50a] (**Scheme 15**). In 2002, Decken *et al.* modified this procedure in the case of fluorene

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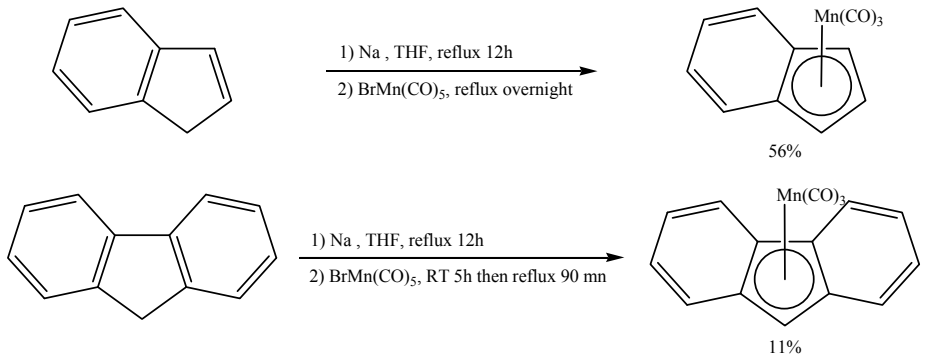
Organometallic Chemistry II; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, pp 469-547; (d) M. J. Morris, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; J. A. Labinger, M. J. Winter, Vol. Eds.; Pergamon: Oxford, UK, **1995**; *Vol. 5*, pp 501-504; (e) M. F. Semmelhack, *Comprehensive Organometallic Chemistry II, Vol. 12*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; p p 1017; (f) F. Rose-Munch, E. Rose, *Curr. Org. Chem.*, **1999**, *3*, 445; (g) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.*, **1999**, *28*, 187; (h) A. Berger, J.-P. Djukic, J.-P. Michon, *C. Coord. Chem. Rev.* **2002**, *225*, 215; (i) F. Rose-Munch, E. Rose, *Eur. J. Inorg. Chem.* **2002**, 1269; (j) E. P. Kündig, S. H. Pache, Arene Organometallic Complexes of Chromium, Molybdenum and Tungsten. In *Science of Synthesis*; T. Imamoto, Ed.; Thieme: Stuttgart, Germany, **2002**; *Vol. 2*, p 155; (k) M. F. Semmelhack, A. Chlenov, *Top. Organomet. Chem.* **2004**, *7*, 21; (l) K. H. Dötz, J. Stendel Jr., In *Modern Arene Chemistry*; D. Astruc, Ed.; Wiley-VCH: Weinheim, **2002**; pp250-296; (m) K. H. Dötz, H. C. Jahr, *Chem. Rec.* **2004**, *4*, 61. (n) A. Minatti, K. H. Dötz, *Top. Organomet. Chem.*, **2004**, *13*, 123; (o) Dötz, K. H.; Wenzel, B.; Jahr, H. C. *Top. Curr. Chem.* **2004**, *248*, 63-103; (p) M. J. McGlinchey, Y. Ortin, C. M. Seward, Chromium Compounds with CO or Isocyanides. In *Comprehensive Organometallic Chemistry III*; R. H. Crabtree, D. M. P. Mingos, Eds.; Elsevier Science Ltd: Oxford, UK, **2006**; *Vol 5*, p 201.

[59] (a) M. F. Semmelhack, *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 12*, Chapter 9, p 979; (b) K. F. McDaniel, In *Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon Press: Oxford, UK, **1995**; *Vol. 6*, pp 93; (c) R. D. Pike, D. A. Sweigart, *Coord. Chem. Rev.* **1999**, *187*, 183; (d) K. Oshima, Organometallic Complexes of Manganese. In *Science of Synthesis*; T. Imamoto, Ed.; Thieme: Stuttgart, Germany, **2002**; *Vol. 2*, p 13. (e) F. Rose-Munch, E. Rose, In *Modern Arene Chemistry*; D. Astruc, Ed.; Wiley-VCH: New-York, **2002**, ch. 11, p 368; (f) D. A. Sweigart, J. A. Reingold, S. U. Son, Manganese Compounds with CO Ligands. In *Comprehensive Organometallic Chemistry III*; R. H. Crabtree, D. M. P. Mingos, Eds.; Elsevier Science Ltd: Oxford, UK, **2006**; *Vol 5*, p 761

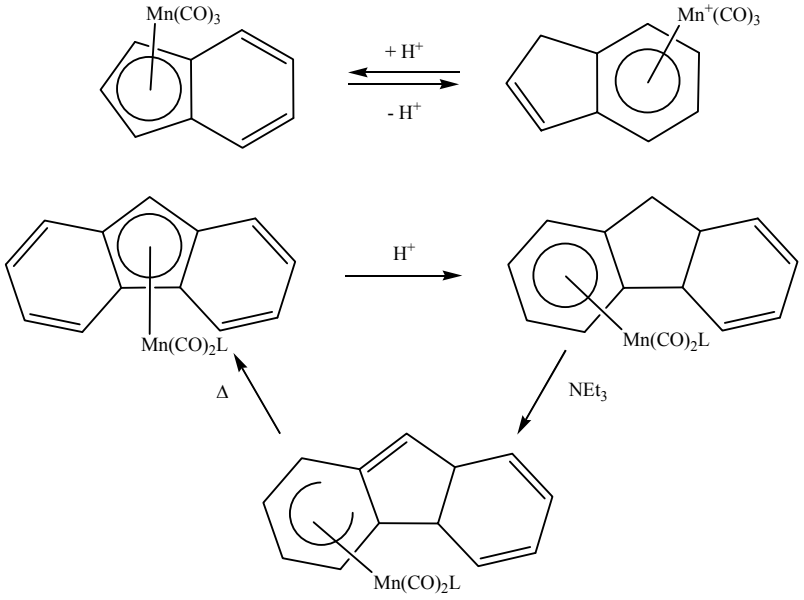
[60] (a) R. B. King, A. Efraty, *J. Organomet. Chem.*, **1970**, *23*, 527; (b) P. M. Treichel, J. W. Johnson, *Inorganic Chemistry*, **1977**, *16 (4)*, 749; (c) M. G. Yezernitskaya, B. V. Lokshin, V. I. Zdanovich, I. A. Lobanova, N. E. Kolobova, *Journal of Organometallic Chemistry*, **1982**, *234*, 329; (d) M. E. Resek, F. Basolo, *Organometallics*, **1984**, *3*, 647; (e) M. G. Yezernitskaya, B. V. Lokshin, V. I. Zdanovich, I. A. Lobanova, N. E. Kolobova, *Journal of Organometallic Chemistry*, **1985**, *282*, 363; (f) R. N. Biagioni, A. D. Luna, J. L. Murphy, *J. Organomet. Chem.*, **1994**, *476*, 183; (g) L. F. Veiros, *J. Organomet. Chem.*, **1999**, *587*, 221; (h) L. F. Veiros, *Organometallics*, **2000**, 19, 3127; (i) A. Decken, A. J. MacKay, M. J. Brown, F. Bottomley, *Organometallics*, **2002**, *21*, 2006; (j) F. Pammer, Y. Sun, C. May, G. Wolmershäuser, H. Kelm, H.-J. Krüger, W. R. Thiel, *Angew. Chem.* **2007**, *119*, 1293.

with the use of *n*-butyl lithium as a base at -78°C to room temperature to obtain the desired complex in 30% yield and studied the pathway of the reaction.[50i]



Scheme 15: Synthesis of (η^5-Cp-ligands)$Mn(CO)_3$ complexes by Efraty and King

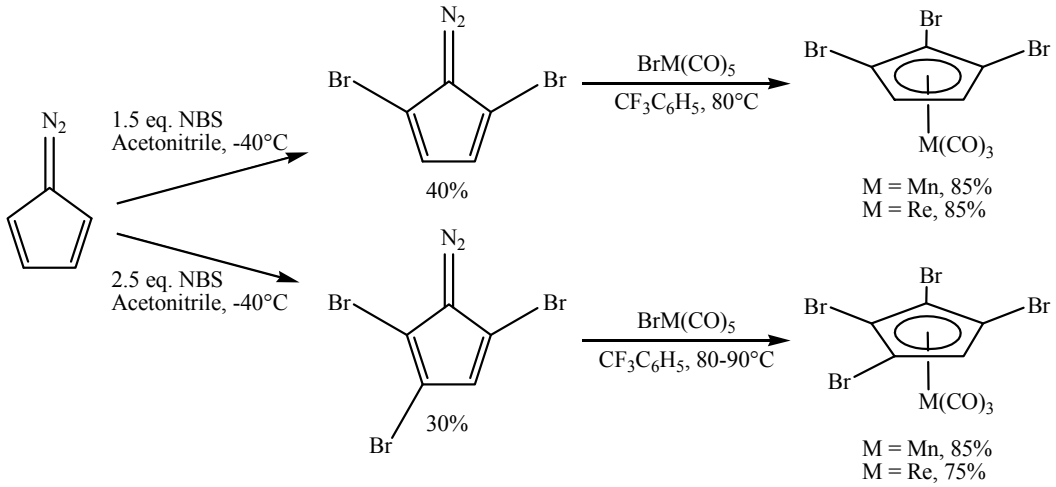
Syntheses and reversible metallotropic rearrangements of (η^5-Cp-ligand)$Mn(CO)_3$ and (η^5-Cp-ligand)$Mn(CO)_2L$ complexes (L = phosphines and phosphites) were also performed in which the metal carbonyl group migrates from the five- to six-membered ring of the aromatic ligand (**Scheme 16**).[50b-h]



Scheme 16: η^6- to η^5-ring slippage reactions in (Cp-ligand)$Mn(CO)_2L$ complexes (L = CO, phosphines and phosphites)

Interesting syntheses of manganese and rhenium polybromo-cyclopentadienyl complexes have been recently described by Gladysz *et al.* (**Scheme 17**).[61] It has been proved in the case of the 2,3,5-tribromodiazocyclopentadiene that the mechanism provides a metal-η^1-tetrabromocyclopentadienyl intermediate which subsequently undergoes a sigmatropic shift to yield the desired complex.

[61] L. V. Dinh, F. Hampel, J. A. Gladysz, *J. Organomet. Chem.*, **2005**, *690*, 493.



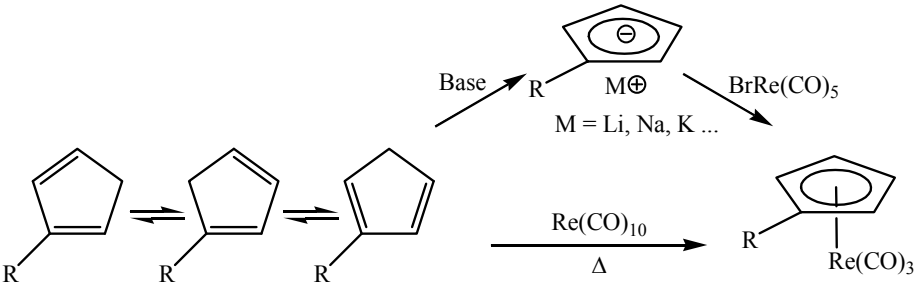
Scheme 17: Syntheses of rhenium and manganese η^5-1,2,3-tribromo- and tetrabromocyclopentadienyl complexes

4.3 Rhenium complexes

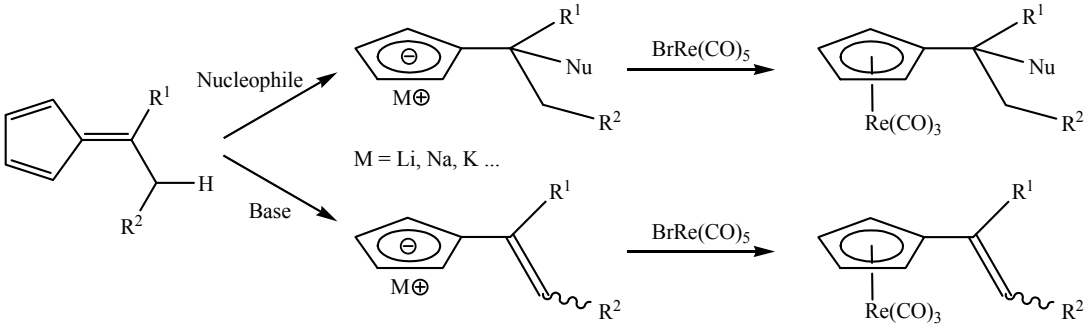
Syntheses of (η^5-Cp-ligand)$Re(CO)_3$ complexes have rarely been reported.[62] The best known organometallic route to the [(η^5-Cp)$Re(CO)_3$]-substituted compounds is the reaction of the cyclopentadienide salt with $BrRe(CO)_5$ or by direct reaction of $Re_2(CO)_{10}$ with the cyclopentadiene at high temperature (**Scheme 18**).[53a,b] An alternative to the use of the low-stable substituted-cyclopentadienes isomers is the fulvene route (**Scheme 19**).[53h] These complexes attached to biomolecules are of great interest in the bioorganometallic chemistry as potential radiopharmaceuticals.[63]

[62] (a) C. P. Casey, M. A. Andrews, D. R. McAlister,J. E. Rinz, *J. Am. Chem. Soc.*, **1980**, *102*, 1927; (b) W. Tam, G.-Y. Lin, W.-K. Wong, W. A. Kiel, V. K. Wong, J. A. Gladysz, *J. Am. Chem. Soc.*, **1982**, *104*, 141; (c) N. M. Boog, H. D. Kaesz, Technetium and Rhenium. In *Comprehensive Organometallic Chemistry*; G. Wilkinson, G. F. A. Stone, E. W. Abel, Eds.; Pergamon Press: Oxford, U.K., **1982**; *Vol. 4*, pp161-242; (d) S. Top, H. El Hafa, A. Vessières, J. Quivy, J. Vassermann, D. W. Hughes, M. J. McGlinchey, J.-P. Mornon, E. Thoreau, G. Jaouen, *J. Am. Chem. Soc.* **1995**, *117*, *7*, 8372 and references herein; (e) W. A. Herrmann, M. R. Geisberger, F. E. Kühn, G. R. J. Artus, E. Herdtweck, *Z. Anorg. Allg. Chem.*, **1997**, *623*, 1229; (f) F. Minutolo, J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **1998**, *120*, 4514; (g) A. J. Arce, R. Machado, Y. De Sanctis, R. Isea, R. Atencio, A. J. Deeming, *J. Organomet. Chem.*, **1999**, *580*, 339; (h) F. Le Bideau, B. El Kaloun, P. Haquette, U. Kernbach, J. Marrot, E. Stephan, S. Top, A. Vessières, G. Jaouen, *Chem. Comm.*, **2000**, 211; (i) P. A. Deck, F. R. Fronczeck, *Organometallics*, **2002**, *19*, 327; (j) F. Le Bideau, J. Hénique, P. Pigeon, J.-M. Joerger, S. Top, G. Jaouen, *J. Organomet. Chem.*, **2003**, *668*, 140.

[63] (a) *Technetium and Rhenium in Chemistry and Nuclear Medicine*; M. Nicolini, G. Bandoli, U. Mazzi, Eds.; Raven Press: New York, **1990**; (b) K. Schwochau, *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 2258; (c) P. A. Schubiger, R. Alberto, A. Smith, *Bioconjugate Chem.* **1996**, *7*, 165; (d) R. K. Hom, J. A. Katzenellenbogen, *Nucl. Med. Biol.*, **1997**, *24*, 485; (e) E. S. Mull, V. J. Sattigeri, A. L. Rodriguez, J. A. Katzenellenbogen, *Bioorg. Med. Chem.*, **2002**, *10*, 1381.



Scheme 18: Cyclopentadiene route to (η^5-Cp-ligand)$Re(CO)_3$ complexes

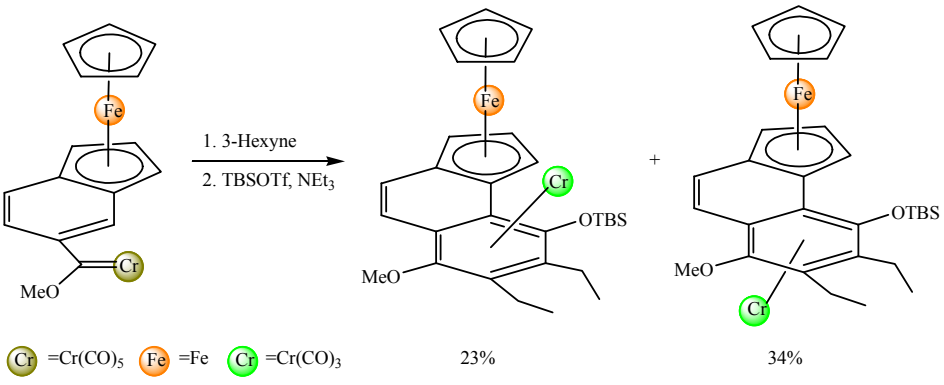


Scheme 19: Fulvene route to (η^5-Cp-ligand)$Re(CO)_3$ complexes

5. Synthesis of heterobimetallic complexes

5.1 Iron-chromium heterobimetallic complexes

In 2005, Dötz *et al.* developed a novel synthesis of heterobimetallic fused-arene complexes: a chromium-templated benzannulation of a ferrocene-type metal carbene (**Scheme 20**).[64] Two diastereomeric benzannulation products were formed, characterized by their *syn*- and *anti*-facial arrangement with respect to their metal moieties and by different anionic peak potentials indicating a distinct influence of the relative stereochemistry on the hetero-metal-metal interaction.

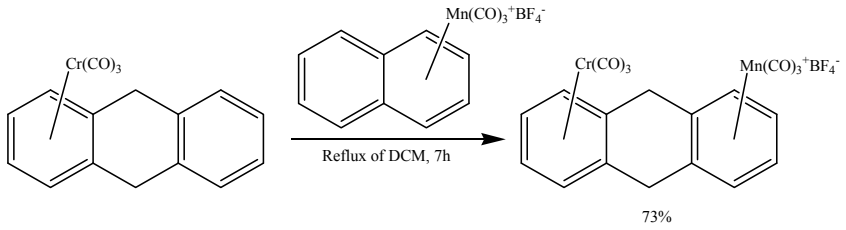


Scheme 20: Chromium-templated benzannulation of indenylcarbene complexes

[64] (a) J. Bennewitz, M. Nieger, B. Lewall, K. H. Dötz, *J. Organ. Chem.*, **2005**, *690*, 5892; (b) J. Bennewitz, Dissertation, University of Bonn, July **2007**.

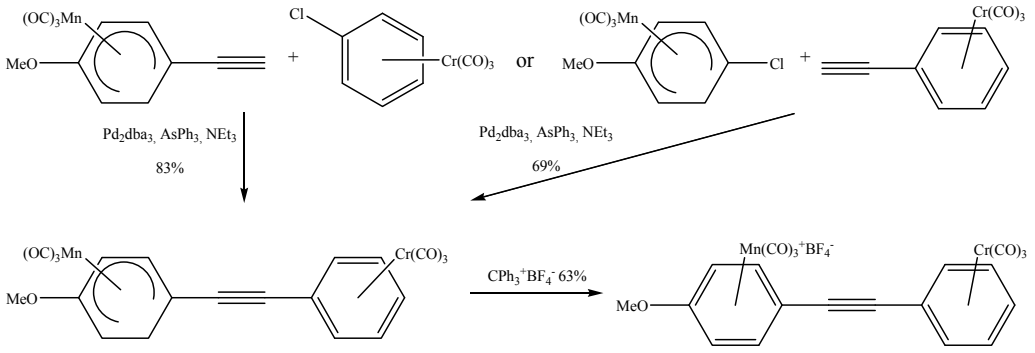
5.2 Manganese-chromium heterobimetallic complexes

One of the reasons why there are only a few publications dealing with these π-hydrocarbon-bridged chromium-manganese heterobinuclear complexes is due to the relative difficulty of finding a strategy for the synthesis of these compounds. A rare example of tricarbonylmanganese-tricarbonylchromium complexes was presented by Chung *et al.*[65] in 1996. They used a manganese tricarbonyl transfer agent, the (η^6-naphthalene)$Mn^+(CO)_3BF_4^-$, to complex the cationic manganese moiety to different ("diarene")$Cr(CO)_3$ complexes (**Scheme 21**). The first limitation of this strategy is the use of the common ligand: it can only be a "diarene". Although there are a large range of available "diarenes" (biphenyl, xanthene, diphenylethylene, stilbene etc.) this has the disadvantage of dismissing fused arenes like phenanthrene, anthracene etc. The second limitation is the use of a cationic manganese moiety which is purified only by crystallisation and consequently minimizes the range of applicable chemical reactions.



Scheme 21: Preparation of the heterobimetallic chromium-manganese (η^6-9,10-dihydroanthracene) complex

In 2004, Rose *et al.*[66] developed a new synthesis of heterobimetallic Cr-Mn-complexes based on a palladium-catalysed Sonogashira coupling reaction. Two routes can lead to the desired binuclear 1-[η^6-phenylethynyl]tricarbonylchromium-[η^5(1-5)-methoxycyclohexa-2,4-dienyl]tricarbonylmanganese complex, which can subsequently undergo an hydride abstraction to yield the corresponding heterobimetallic η^6-Cr-η^6-Mn complex (**Scheme 22**). This acyclic conjugated π-system allows the reversible η^5/η^6-manganese transformation and offers a possible electronic interaction between the two metal units through the alkyne.

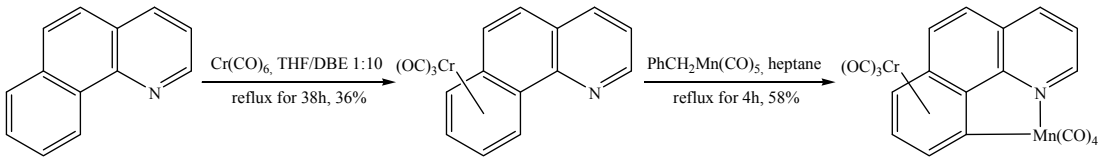


Scheme 22: Palladium-catalysed Sonogashira coupling reaction leading to a binuclear chromium-manganese complex

[65] S. S. Lee, T.-Y. Lee, J. E. Lee, Y. K. Chung, M. S. Lah, *Organometallics*, **1996**, *15*, 3664.
[66] S. Schouteeten, J.-P. Tranchier, F. Rose-Munch, E. Rose, A. Auffrant, G. R. Stephenson, *Organometallics*, **2004**, *23*, 4308.

5.3 Cyclomanganated tricarbonylchromium complexes

In the case of *N*-heteroarenes, the manganese atom can coordinate the ligand in a different manner to form five-membered metallacycles complexes.[67] In this regard, the synthesis of the cyclomanganated (η^6-benzo[*h*]quinoline)tricarbonylchromium complex, which was first reported by Bruce and co-workers[68] and extended later by Djukic and Pfeffer[69] involves two steps (**Scheme 23**). First the chromium moiety is introduced by the direct reaction of $Cr(CO)_6$ on benzo[*h*]quinoline which leads to a single regioisomer. Subsequently the *ortho*-manganation of the chromium complex with the use of benzylpentacarbonylmanganese involves a C-H activation that yields the desired heterobinuclear compound.



Scheme 23: Synthesis of cyclomanganated (η^6-benzo[*h*]quinoline)tricarbonylchromium

6. Aim of the work

The aim of this work is the synthesis of novel heterobimetallic chromium-manganese or chromium-rhenium complexes containing fused-ring arenes in order to study the tuning of the haptotropic tricarbonylchromium migration by the introduction of the second metal moiety. Preferentially the chromium moiety has to be introduced via the chromium-templated-[3+2+1] benzannulation. The straightforward and regioselective synthesis of arene-$Cr(CO)_3$ complexes via the benzannulation reaction is the method of choice to study the haptotropic phenomenon: under mild conditions it always affords the kinetic products which can subsequently undergo a thermo-induced migration to provide the corresponding thermodynamically stable haptotropomers. The introduction of a second metal moiety might give to the complexes specific properties aroused by possible interactions between the two metal centers and may influence the metallotropic rearrangement along one face of the arene skeleton.

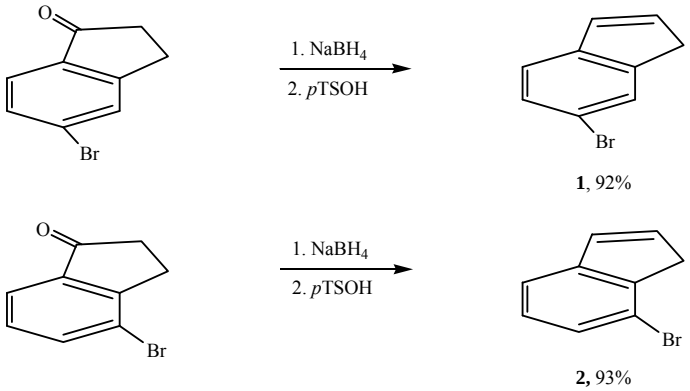
[67] T. C. Flood In *Comprehensive Organometallic Chemistry*, Pergamon: Oxford, U.K., **1995**; *Vol. 6*, pp 21-86
[68] M. I. Bruce, B. L. Goodall, F. G. A. Stone, *J. Organomet. Chem.*, **1973**, *60*, 343.
[69] (a) J. P. Djukic, A. Maisse, M. Pfeffer, A. de Cian, J. Fischer, *Organometallics*, **1997**, *16*, 657; (b) J. P. Djukic, A. Maisse, M. Pfeffer, *J. Organomet. Chem.* **1998**, *567*, 65; (c) J. P. Djukic, A. Maisse, M. Pfeffer, K. H. Dötz, M. Nieger, *Eur. J. Inorg. Chem.* **1998**, 1781; (d) J. P. Djukic, A. Maisse, M. Pfeffer, K. H. Dötz, M. Nieger, *Organometallics*, **1999**, *18*, 2786.

III] RESULTS AND DISCUSSION

1. Benzo[*e*]indene-Mn-Cr systems

1.1 Synthesis of the starting ligands

The syntheses of the two conformers - 6-bromo-1*H*-indene **1** and 7-bromo-1*H*-indene **2** - are described in parallel as well as all the following syntheses of this first part. The precursors are the 5-bromo-1-indanone and the 4-bromo-1-indanone. The ketones undergo a quantitative reduction by sodium tetrahydrid boron at room temperature overnight to yield to the corresponding alcohols which are submitted to a dehydratation with *para*-toluene sulfonic acid in toluene at 115°C for ninety minutes. Ligand **1** and ligand **2** are respectively obtained in 92 and 93 % isolated yields over the two steps (**Scheme 24**). The ^{1}H-NMR and the ^{13}C-NMR of compounds **1** and **2** are almost identical.



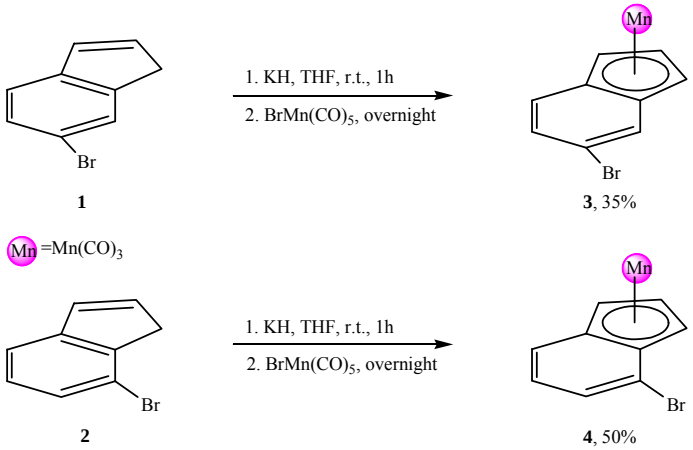
Scheme 24: Synthesis of the starting ligands **1** and **2**

1.2 Manganese complexation of the bromoindene ligands

1.2.1 Synthetic procedure

The complexation of the manganese moiety on indene was already reported in the literature but not with bromoindene.[70] The significant difference is that *n*-butyl lithium cannot be used as a base in the case of bromoindene because of the competition with the lithium-halide exchange (which will be used later in the synthesis of the Fischer carbene). That is the reason why potassium hydride is the reactant of choice for this acid-base reaction. Furthermore, the use of this compound allows milder conditions, at room temperature instead of -78°C as reported in the literature with *n*-butyl lithium. After one hour the pentacarbonylmanganese bromide can be added to the solution and stirred overnight at room temperature to give the corresponding tricarbonyl-[η^{5}-1,2,3,3a,7a-(6-bromoindenyl)]manganese complex **3** and tricarbonyl-[η^{5}-1,2,3,3a,7a-(7-bromoindenyl)]manganese **4** in 35 to 50% yields (**Scheme 25**).

[70] (a) R. B. King, A. Efraty, *J. Organomet. Chem.*, **1970**, *23*, 527; (b) A. Decken, A. J. MacKay, M. J. Brown, F. Bottomley, *Organometallics*, **2002**, *21*, 2006.



Scheme 25: Manganese complexation of the bromoindene ligands **1** and **2**

1.2.2 Spectroscopic analysis of **3**

The IR-spectrum of **3** (in petroleum ether) shows the two characteristic bands of the manganese carbonyl ligands at 2026 (s) and 1949 (vs) cm^{-1}. The ^{1}H-NMR indicates that the manganese complexation leads first to the disappearance of the typical signal at 3.2 ppm of the methylene group and the disappearance of the ethylenic protons signal around 6.4 and 6.7 ppm to give three signals shifted around 5.3 and 5.5 ppm. The ^{13}C-NMR represents the three tertiary carbons of the complexed Cp-ring with two signals around 70 ppm and one around 90 ppm. The signals of the two bridging carbons are also strongly shifted, from around 140 ppm to around 100 ppm. As for the three other tertiary carbon atoms of the Ph-ring and the quaternary carbon bearing the bromide, they remain nearly constant. The characteristic manganese carbonyls appear at 224.9 ppm. FAB mass spectroscopy shows the ion-molecule's peak at 331.9 with an intensity of 54%. The peaks at 303.9 (41%), 277.9 (99%) and 247.9 (64%) correspond successively to the loss of the three manganese carbonyl ligands.

1.2.3 Spectroscopic analysis of **4**

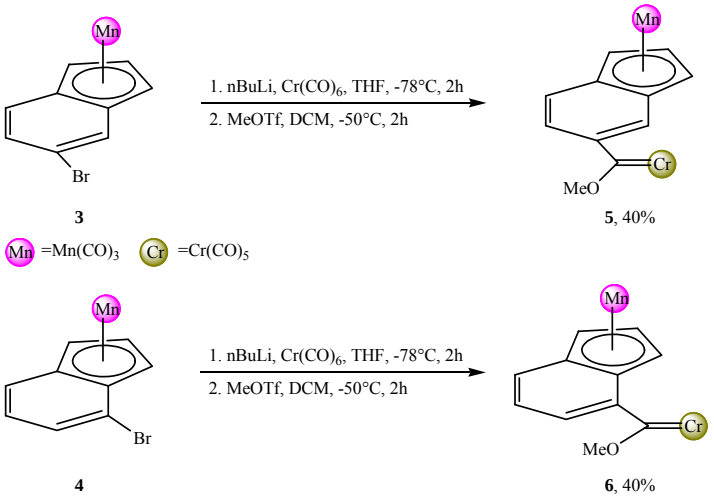
IR-spectroscopy (in petroleum ether) shows the typical bands of the manganese carbonyl ligands at 2028 (s) and 1946 (vs) cm^{-1}. The ^{1}H-NMR indicates that the complexed cyclopentadienyl ring leads to three signals between 5.12 and 5.37 which characterize the complexation of the manganese moiety. In ^{13}C-NMR, the results are similar to those for compound **3,** with two signals around 72 ppm and one at 89 ppm for the complexed ring, the shift of the bridging carbons and the new signal at 224.6 ppm corresponding to the manganese carbonyls signal. FAB mass spectroscopy shows the ion-molecule's peak at 331.8 with an intensity of 13%. The peaks at 303.8 (6%), 275.9 (21%) and 247.9 (99%) correspond successively at the loss of the three manganese carbonyl ligands. The peak at 192.9 (3%) shows the decoordinated ligand.

1.3 Fischer carbene synthesis with the tricarbonyl(bromoindenyl)-manganese complexes 3 and 4

1.3.1 Synthetic procedure

The synthesis method for the Fischer-carbene on the tricarbonyl(bromoindenyl)manganese complexes follows the so-called Fischer-route. The lithium-bromide exchange occurs at -

78°C in THF under argon without any competition with a potential attack of *n*-butyl lithium on the carbonyls of the manganese and is immediately followed by an addition of $Cr(CO)_6$ on the compound. The carbonylate is then protected by a methyl group via a strong methylation's agent - the methyl triflate - at -50°C in DCM to afford **5** and **6** in 40% isolated yield (**Scheme 26**). There is no decomposition of the manganese complex during the process.



Scheme 26: Fischer carbene synthesis of cymanthrene-type complexes

1.3.2 Spectroscopic analysis of **5**

The IR-spectrum of **5** (in petroleum ether) shows the same tricarbonylmanganese signals at 2027 (s) and 1947 (s) cm^{-1} as in complex **3** and two new bands for the Fischer carbene carbonyls at 2063 (m) and 1955 (s) cm^{-1} for A1 and E. These results imply that the Fischer carbene does not interfere with the electronic environment of the manganese moiety. The ^{13}C-NMR-spectrum of **5** shows the characteristic Fischer carbene signals and its carbonyls at 216, 224.2 and 348.5 ppm whereas the other signals remain nearly the same according to compound **3**. FAB mass spectroscopy represents the ion-molecule's peak at 487.9 with an intensity of 19%. The peaks at 431.9 (54%), 403.9 (30%), 375.9 (99%), 347.9 (75%) and 263.9 (8%) correspond successively at the loss of two, three, four, five and eight carbonyl ligands.

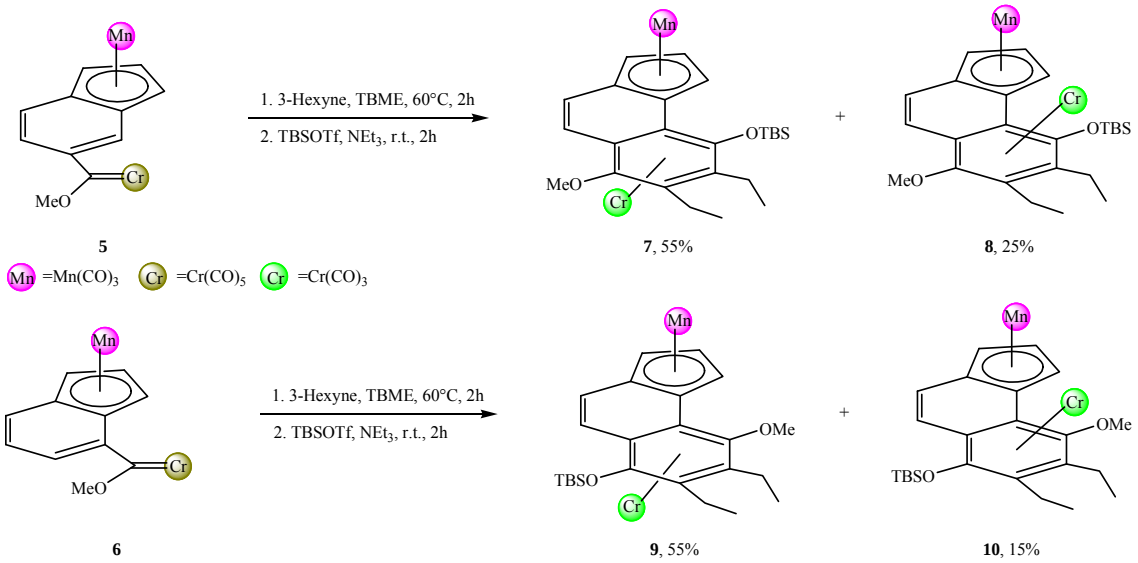
1.3.3 Spectroscopic analysis of **6**

IR-spectroscopy of **6** (in petroleum ether) shows the unchanged tricarbonylmanganese signals at 2027 (m) and 1954 (s) cm^{-1} and the new signals at 2064 (m) and 1954 (s) cm^{-1}, just like for compound **5**. The ^{13}C Fischer carbene characterized signals are easily identifiable at 217.1, 225.2 and 347.1 ppm. FAB mass spectroscopy shows the ion-molecule's peak is present at 487.9 with an intensity of 10%. The peaks at 459.9 (3%), 431.9 (12%), 403.9 (27%), 375.9 (23%), 347.9 (89%), 320.0 (13%), 292.0 (97%), and 264.0 (100%) correspond successively at the loss one by one of all of the eight carbonyl ligands.

1.4 Benzannulation reaction of the (Fischer carbene)-tricarbonylmanganese complexes 5 and 6

1.4.1 Synthetic procedure

The first heterobimetallic chromium-manganese oligocyclic-fused-arene complexes are synthesized via the chromium-templated benzannulation of the Fischer aryl carbenes. The two different Fischer carbenes **5** and **6** in the presence of 3-hexyne in an ethereal solvent at 60°C for two hours provide each densely substituted phenols; subsequently the phenolic functions are protected at room temperature with a *tert*-butyl-dimethyl-silyl group. After a chromatographic column of each reaction, *syn*-**7** and *syn*-**9** and *anti*-diastereoisomers **8** and **10** of the heterobimetallic complexes are purified; *anti*-isomers are in both cases the major isomers (**Scheme 27**). The benzannulation is regiospecific and affords the angular annulation products **7**-**10**,[71] as established by ^{1}H-NMR-spectroscopy and X-Ray analysis.



Scheme 27: Benzannulation of the (Fischer carbene)-tricarbonylmanganese complexes **5** and **6**

1.4.2 Spectroscopic analysis of **7**

The IR-spectroscopy of **7** (in petroleum ether) shows the two manganese bands unchanged at 2025 (vs) and 1948 (s) cm^{-1} and the new tricarbonylchromium bands at 1963 (vs), 1903 (m) and 1890 (m) cm^{-1}. The ^{1}H-NMR represents new signals corresponding to the new benzannulated product between 0.48 and 3.78 ppm. The ^{13}C-NMR shows the carbonyls signals at 224.9 ppm for $Mn(CO_3)$ and at 234.0 ppm for $Cr(CO_3)$. EI mass spectroscopy shows the ion-molecule's peak at 656.0 with an intensity of 15%. The peak at 598.9 (4%) and 572.0 (39%) represents the compound minus two and three carbonyl ligands, at 520.1 (10%) is shown the loss of the tricarbonylchromium, at 488.0 (41%) is the compound minus six carbonyl ligands, at 436.1 (100%) there is the loss of the chromium moiety and the three manganese carbonyls and finally at 382.2 (14%) is represented the compound without any metal moiety.

[71] M. F. Semmelhack, S. Ho, D. Cohen, M. Steigerwald, M. C. Lee, G. Lee, A. M. Gilbert, W. D. Wulff, R. G. Ball, *J. Am. Chem. Soc.*, **1994**, *116*, 7108.

Red crystals of **7** are grown at 4°C from dichloromethane (**Figure 7**). The torsion angle φ between the two coordinated aromatic rings is null which indicates that the compound is not distorted by the successive metal complexations. As indicated by the three dihedral angles α1, α2 and α3, the $Cr(CO)_3$ tripod is neither eclipsed nor staggered but in between. The Mn-C bonds are all about 0.1 Å shorter than the Cr-C bonds.

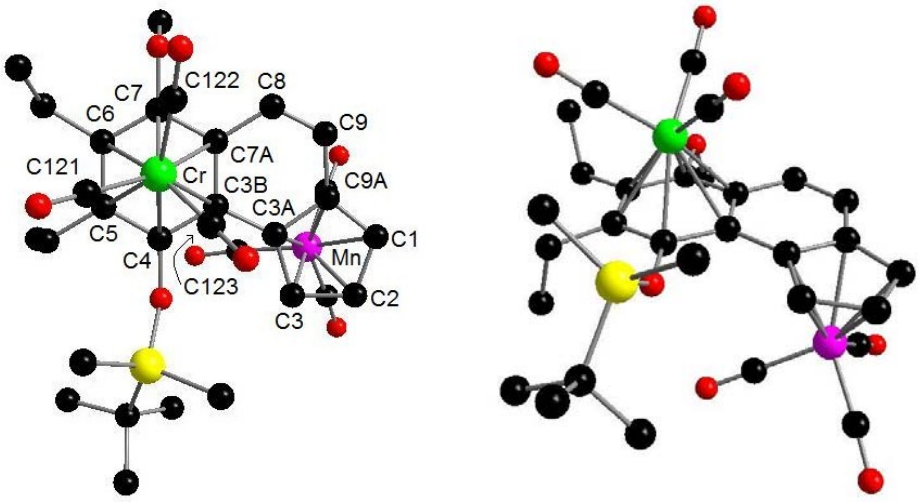


Figure 7. Molecular structure of the *anti*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-6-methoxy-9-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese complex **7.** The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The three dihedral angles are α1 (C5-$Cr_{proj.}$-Cr-C121) = -15.08(2)°, α2 (C7-$Cr_{proj.}$-Cr-C122) = -13.16(2)° and α3 (C3B-$Cr_{proj.}$-Cr-C123) = -13.91(2)°, Cr_{proj} is the projection of the chromium atom on the aromatic plane. The torsion angle is φ (C3-C3A-C3B-C4) = -0.45(1)°. Selected bond lengths (Å): Mn-C1 2.14(0), Mn-C2 2.12(0), Mn-C3 2.12(0), Mn-C3A 2.18(0), Mn-C9A 2.19(0), Cr-C4 2.25(0), Cr-C5 2.26(0), Cr-C6 2.25(0), Cr-C7 2.21(0), Cr-C7A 2.26(0), Cr-C3B 2.29(0).

1.4.3 Spectroscopic analysis of **8**

IR-spectrum of **8** (in petroleum ether) shows the two manganese bands almost unchanged at 2031 (vs) and 1946 (m) cm^{-1} and the three tricarbonylchromium bands at 1965 (s), 1890 (w) and 1886 (m) cm^{-1}. There is a slight difference between the two isomers *anti* **7** and *syn* **8** but not significant enough in order to link it to physico-chemical properties. The ^{1}H-NMR and ^{13}C-NMR spectra of complex **8** are very similar to those of the isomer **7**. EI mass spectroscopy shows the ion-molecule's peak at 656.0 with an intensity of 19%. The peak at 572.0 (7%) represents the compound minus three carbonyl ligands, at 520.0 (9%) is shown the loss of the tricarbonylchromium, at 488.0 (6%) is the compound minus six carbonyl ligands, at 436.1 (100%) there is the loss of the chromium moiety and the three manganese carbonyls and finally at 382.2 (2%) is represented the compound without any metal moiety.
Red crystals of **8** are grown at 4°C from dichloromethane (**Figure 8**). The torsion angle φ between the two coordinated aromatic rings is not null which indicates that contrary to complex **7** a helical twist is imposed on the compound by the *syn*-facial arrangement of the two metal units. As indicated by the three dihedral angles α1, α2 and α3, the $Cr(CO)_3$ tripod is eclipsed with respect to the OTBS group, in contrast with the conformation found for complex **7**.

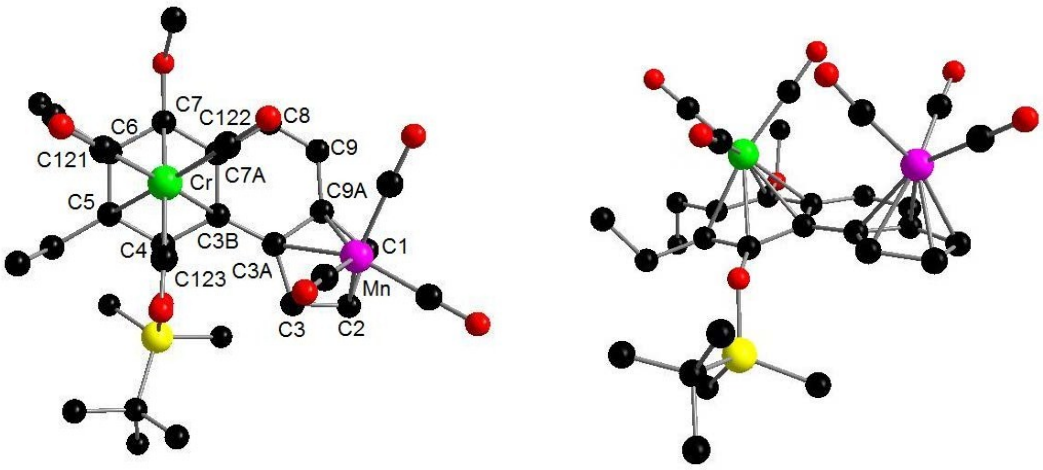


Figure 8. Molecular structure of the *syn*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-6-methoxy-9-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese complex **8.** The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C6-$Cr_{proj.}$-Cr-C121) = 2.87(2)°, α2 (C7A-$Cr_{proj.}$-Cr-C122) = 1.65(2)° and α3 (C3B-$Cr_{proj.}$-Cr-C123) = -0.93(3)°. The torsion angle is φ (C3-C3A-C3B-C4) = -13.98(1)°. Selected bond lengths (Å): Mn-C1 2.13(0), Mn-C2 2.12(0), Mn-C3 2.15(0), Mn-C3A 2.23(0), Mn-C9A 2.18(0), Cr-C4 2.27(0), Cr-C5 2.25(0), Cr-C6 2.21(0), Cr-C7 2.26(0), Cr-C7A 2.31(), Cr-C3B 2.24(0).

1.4.4 Spectroscopic analysis of **9**

IR-spectrum of **9** (in petroleum ether) indicates the $Mn(CO)_3$ bands at 2025 (s), and 1948 (vs) cm^{-1} and the $Cr(CO)_3$ at 1963 (A1, vs), 1901 (E, m) and 1890 (E, m) cm^{-1}.The ^{1}H-NMR and ^{13}C-NMR are similar to those presented previously for compounds **7** and **8**. EI mass spectroscopy shows the ion-molecule's peak is present at 656.1 with an intensity of 4.5%. The peak at 572.1 (13.5%) represents the compound minus three carbonyl ligands, at 520.2 (14%) is shown the loss of the tricarbonylchromium, at 488.1 (17%) is the compound minus six carbonyl ligands, at 436.2 (99%) there is the loss of the chromium moiety and the three manganese carbonyls and finally at 382.0 (4%) is represented the compound without any metal moiety.
Red crystals of **9** are grown at 4°C from dichloromethane (**Figure 9**). Like in complex **7**, the torsion angle φ between the two coordinated aromatic rings is null which indicates that the compound is not distorted by the successive metal coordinations. As indicated by the three dihedral angles α1, α2 and α3, the $Cr(CO)_3$ tripod is almost eclipsed with respect to the OTBS group.

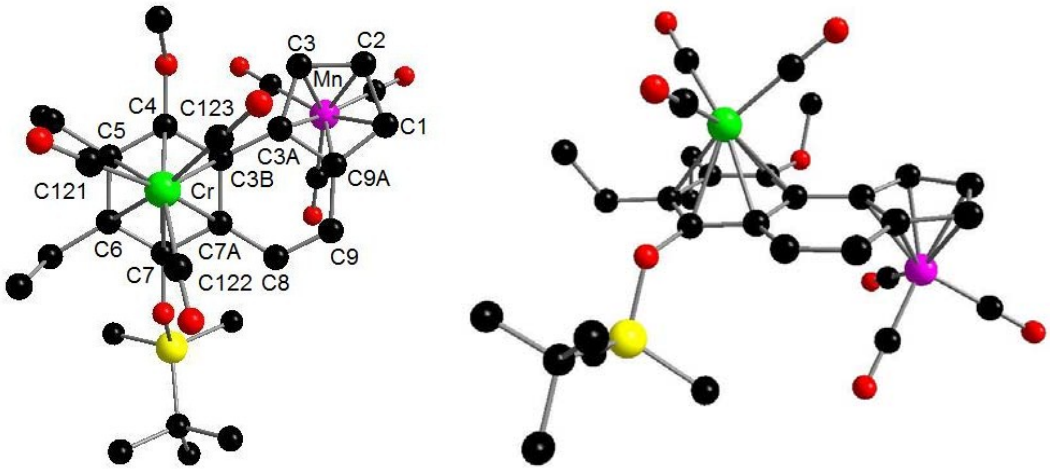


Figure 9. Molecular structure of the *anti*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-9-methoxy-6-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese complex **9.** The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C5-Cr$_{proj.}$-Cr-C121) = 10.12(1)°, α2 (C7-Cr$_{proj.}$-Cr-C122) = 13.22(1)° and α3 (C3B-Cr$_{proj.}$-Cr-C123) = 11.47(0)°. The torsion angle is φ (C3-C3A-C3B-C4) = 0.48°. Selected bond lengths (Å): Mn-C1 2.15(0), Mn-C2 2.13(0), Mn-C3 2.13(0), Mn-C3A 2.17(0), Mn-C9A 2.18(0), Cr-C4 2.24(0), Cr-C5 2.23(0), Cr-C6 2.26(0), Cr-C7 2.28(0), Cr-C7A 2.24(0), Cr-C3B 2.25(0).

1.4.5 Spectroscopic analysis of **10**

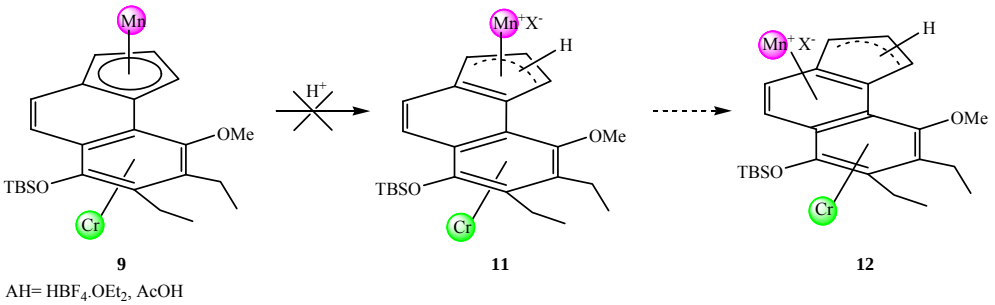
The IR-spectrum of **10** (in petroleum ether) indicates the $Mn(CO)_3$ peaks at 2026 (s) and 1950 (s) cm^{-1} and the $Cr(CO)_3$ peaks at 1970 (s), 1912 (m) and 1900 (m) cm^{-1}. As previously, the ^{1}H-NMR and ^{13}C-NMR look similar. EI mass spectroscopy shows the ion-molecule's peak is present at 656.1 with an intensity of 2%. The peak at 572.1 (15%) represents the compound minus three carbonyl ligands, at 520.2 (12%) is shown the loss of the tricarbonylchromium, at 488.1 (21%) is the compound minus six carbonyl ligands, at 436.2 (99%) there is the loss of the chromium moiety and the three manganese carbonyls and finally at 382.0 (2%) is represented the compound without any metal moiety.

For unexplained reasons, complex **10** is the only compound in all this work that never crystallized, neither in dichloromethane and diethyl ether as usual nor in different polar and apolar solvents.

1.5 Attempt of haptotropic tricarbonylmanganese rearrangement

The rearrangement was tried by protonating the five-membered ring using an acid medium;[72] thus the manganese moiety would become cationic with 16 electrons - complex **11** - and would migrate to the next aromatic ring to remain cationic but with 18 electrons - complex **12** (**Scheme 28**). Unfortunately the protonation does not occur and the heterobimetallic complex **9** starts to decompose after a few hours.

[72] (a) M. G. Yezernitskaya, B. V. Lokshin, V. I. Zdanovich, I. A. Lobanova, N. E. Kolobova, *Journal of Organometallic Chemistry*, **1982**, *234*, 329; (b) M. G. Yezernitskaya, B. V. Lokshin, V. I. Zdanovich, I. A. Lobanova, N. E. Kolobova, *Journal of Organometallic Chemistry*, **1985**, *282*, 363.



9 **11** **12**

AH= $HBF_4.OEt_2$, AcOH

Scheme 28: Attempt of pH-induced haptotropic $Mn(CO)_3$ migration

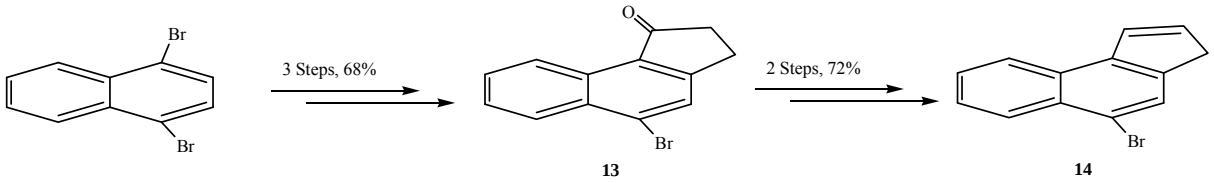
1.6 Discussion/conclusion

With the complexes **7**, **8**, **9** and **10**, novel heterobimetallic tricarbonylchromium-tricarbonylmanganese complexes have been synthesized. A new way of preparing (η^5-Cp-ligand)$Mn(CO)_3$ has been developed with milder conditions and at room temperature. It has been proved that the manganese moiety stands the drastic conditions of the so-called Fisher-route and does not decompose. As expected the benzannulated products are all angular and present a *syn*- and *anti*-configuration, with the *anti*-isomers as the major products. As indicated by the torsion angles, the polyaromatic ligands of the *anti*-isomers describe a plane whereas in the *syn* case a helical twist of the tricyclic arene is induced by the hindrance of the two metal fragments. These primary results are encouraging and lead to follow the research in this direction by building a bigger polyaromatic ligand that could allow a haptotropic migration of the chromium unit.

2. Dibenzo[*c*,*e*]indene-Mn-Cr system

2.1 Synthesis of 8-bromobenzo[*e*]-1*H*-indene 14

The synthesis of the starting material **14** - the 8-bromobenz[*e*]-1*H*-indene - is achieved using a five-step sequence (**Scheme 29**).[73] In the first step, a lithium-bromide exchange of one bromide atom of 1,4-dibromo-naphthalene is performed with *n*-BuLi, followed by an electrophilic attack of trimethylsilyl chloride. The two following steps are inter- and intra-molecular Friedel-Crafts reactions with 3-chloropropionyl chloride, which afford the 5-bromo-2,3-dihydro-benz[e]inden-1-one **13** in an overall yield of 78%. A reduction of the ketone into the secondary alcohol and its dehydration at only 50°C in order to avoid a dimer by-product afford **14** in 72% isolated yield over these two steps. The overall yield from the precursor 1,4-dibromonaphthalene to 8-bromobenzo[*e*]-1*H*-indene **14** is 57%.

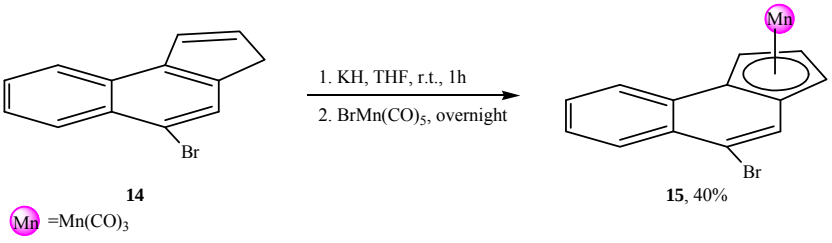


Scheme 29: From 1,4-dibromonaphthalene to 8-bromobenzo[*e*]-1*H*-indene **14**

2.2 Manganese complexation of the 8-bromobenzo[*e*]-1*H*-indene ligand

2.2.1 Synthetic procedure

The complexation of the manganese moiety on the 8-bromobenzo[*e*]-1*H*-indene **14** has not been reported in literature. We follow the procedure described in the first part with the benzo[*e*]-1*H*-indene systems. A tetrahydrofuran solution of 8-bromobenzo[*e*]-1*H*-indene **14** and potassium hydride is stirred at room temperature for one hour (exothermic reaction), and then the bromide-pentacarbonylmanganese powder is added and stirred overnight. Purification under argon on a silica gel chromatography column affords the half-sandwich tricarbonyl-{η^5-1,2,3,3a,9a-(8-bromobenzo[*e*]indenyl)}manganese complex **15** as a yellow powder in 40% yield (**Scheme 30**).



Scheme 30: Synthesis of the tricarbonyl(8-bromobenzo[*e*]indenyl)manganese complex **14**

[73] J. Bennewitz, Dissertation, University of Bonn, July **2007**.

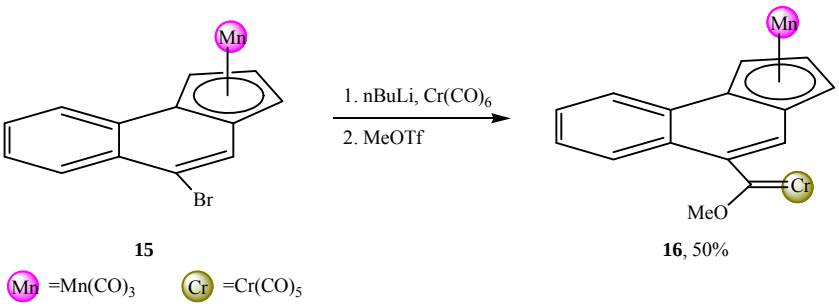
2.2.2 Spectroscopic analysis of **15**

The ^{1}H NMR spectra of **14** and **15** reveal after the metal coordination upfield shifts of 1.4-2.3 ppm for the hydrogen atoms H2-H3 and a downfield shift of about 1.3-1.4 ppm for H1. The cyclopentadiene-carbon atom C1 in the ^{13}C NMR spectra is shifted downfield by 40 ppm whereas the carbons C2 and C3 are shifted upfield by 42-62 ppm and the carbons C3a and C9b are shifted upfield by 40-42 ppm. These data confirm the manganese complexation on a cyclopentadienyl-type ligand. Furthermore, a new signal is present at 224.9 ppm corresponding to the three carbonyl ligands which also appear in the IR-spectrum with two characteristic bands at 2025 (s) and 1946 (vs) cm^{-1}. Mass spectroscopy (FAB) shows the ion-molecule's peak at 282 with an intensity of 25%. The peaks at 325.9 (59%), 297.9 (52%) and 245 (42%) show successively the loss of two then three carbonyl ligands and finally the entire metal moiety.

2.3 Fischer carbene synthesis with the tricarbonyl(8-bromobenzo[*e*]indenyl) manganese complex 15

2.3.1 Synthetic procedure

Following the so-called Fischer-route, the lithium-bromide exchange occurs on **15** at -78°C in THF under argon and is immediately followed by an addition of $Cr(CO)_6$ in the solution. The resulting acyl chromate is protected with methyl triflate at -50°C in DCM to afford **16** as a dark-red powder in 50% yield (**Scheme 31**).
In this synthesis, during the desired bromide-lithium exchange the tricarbonylmanganese stands the drastic conditions of the Fischer-carbene synthesis: no nucleophilic attack of the *n*-butyl lithium on the carbonyls of the manganese is observed.



Scheme 31: Fischer-carbene synthesis of the tricarbonylmanganese complex **2**

2.3.2 Spectroscopic and X-Ray structure analysis of **16**

The reaction can be monitored by IR-spectroscopy with the appearance of the characteristic signals at 2067 (A1, m) and 1957 ("E", vs) cm^{-1}, indication for the acyl chromate formation. The signals relative to the $Mn(CO)_3$ moiety remain the same which indicates that the Fischer carbene does not modify the $Mn(CO)_3$ electronic environment. In the ^{1}H-NMR-spectrum, the singulet methoxy signal appears at 4.34 ppm and the new ^{13}C peaks are in agreement with carbene and carbonyl carbons at 216.2, 224.9 and 356.7 ppm. Mass spectroscopy (EI) shows the ion-molecule's peak at 537.8 with an intensity of 2%. The peaks at 481.9 (13%), 453.9 (3%), 425.9 (18%), 397.9 (82%) 369.9 (8%), 341.9 (28%) and 313.9 (53%) show successively the loss of the eight carbonyl ligands.

Dark red crystals are grown in dichloromethane at 4°C by slow evaporation. Complex **16** crystallizes in the triclinic system and the lattice belongs to the symmetry space group $P\bar{1}$. The benzo[*e*]indene establishes almost a plane with a torsion angle φ (C1-C12-C13-C9) = 1.96(19)°. The average distance between the manganese atom and the five carbon atoms of the cyclopentadienyl ring is 2.15 Å. It is interesting to notice the surprising *syn* position of the Fischer carbene according to the tricarbonylmanganese which is undoubtedly a consequence of the packing effect; NMR-spectra indicate that in solution the Fischer carbene moiety undergoes a free rotation along the C5-C14 bond (**Figure 10**).

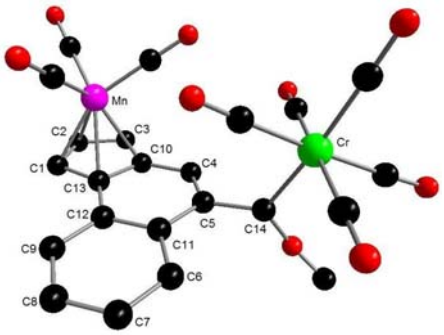
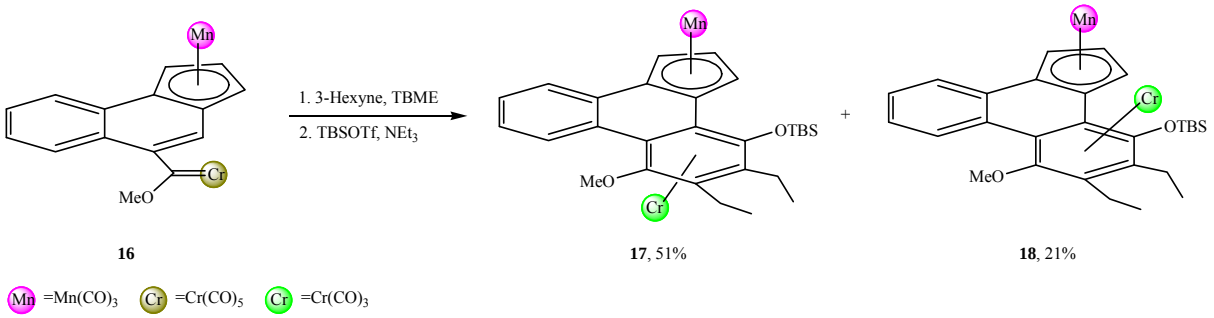


Figure 10. Molecular structure of the tricarbonyl-{pentacarbonyl[8-benzo[*e*]indenyl-(methoxy)carbene]chromium[η^5-1,2,3,3a,9a]}manganese complex **16.** The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The torsion angle is φ (C1-C12-C13-C9) = 1.96(19)°. Selected bond lengths (Å): Mn-C1 2.14(3), Mn-C2 2.12(3), Mn-C3 2.13(3), Mn-C10 2.20(3), Mn-C13 2.19(3).

2.4 Benzannulation reaction of (Fischer carbene)-tricarbonylmanganese complex 16

2.4.1 Synthetic procedure

The two diastereoisomeric *syn*- and *anti*-heterobimetallic chromium-manganese complexes are synthesized via the chromium-templated benzannulation of the Fischer aryl carbenes. The manganese-type chromium carbene **16** in the presence of 3-hexyne in an ethereal solvent at 60°C for two hours provides two densely substituted phenols; subsequently the phenolic functions are protected at room temperature with a *tert*-butyl-dimethylsilyl group. After chromatographic column, *anti*- **17** and *syn*-diastereoisomers **18** complexes are purified, the *anti*-isomer is the major isomer in 51% yield and the *syn*-isomer the minor one in 21% yield (**Scheme 32**).



Scheme 32: Benzannulation of a cymanthrene-type metal carbene complex **16**

Mass spectra of these two compounds in both cases reveal a parent mass and a fragment pattern in which carbonyl ligands are sequentially lost by fragmentation. The ^{1}H and ^{13}C NMR spectra of **17** and **18** appear very similar and are not significantly differentiated in order to observe the two isomers. Furthermore, compounds **17** and **18** give indistinguishable IR ν (CO) bands which reveal that the compounds have identical chemical environments although they are diastereoisomers *syn* and *anti*.

2.4.2 Spectroscopic analysis of **17**

IR-spectroscopy of **17** (in petroleum ether) indicates that the two manganese bands remain unchanged at 2025 (vs) and 1948 (s) cm^{-1} and the tricarbonylchromium presents three bands at 1963 (vs), 1903 (s) and 1888 (s) cm^{-1}. The ^{1}H-NMR spectrum shows that the new phenolic ring protection group singulet signals resonate at 0.40, 0.63 and 1.17 ppm, followed by the two ethyl signals between 1.30 and 3.04 ppm and the methoxy signal at 3.57 ppm. The other part of the spectrum is composed of signals between 5.04 and 6.19 ppm relative to the protons H1-H3, and then signals between 7.51 and 9.01 ppm relative to the aromatic protons H4-H7. The ^{13}C-NMR spectrum represents the new phenolic ring signals of the protecting group and ethyl groups (from -2.1 to 26.3 ppm) and four new quaternary aromatic carbons signals (between 104.3 and 140.7 ppm), as well as the tricarbonylchromium signal at 234.1 ppm. The tricarbonylmanganese signal remains at 224.4 ppm. EI mass spectroscopy shows the ion-molecule's peak at 706.1 with an intensity of 24%. The peak at 622.1 (60%) represents the compound minus three carbonyl ligands, at 566.1 (39%) it shows the loss of the five carbonyl ligands, at 538.1 (79%) is the compound minus six carbonyl ligands, at 486.2 (64%) there is the loss of the chromium moiety and the three manganese's ligands and finally at 425.1 (96%) is represented the compound without any metal moiety.

2.4.3 Spectroscopic analysis of **18**

IR-spectroscopy of **18** (in petroleum ether) also indicates that the two manganese bands remain almost unchanged at 2030 (vs) and 1943 (s) cm^{-1} and the tricarbonylchromium presents three bands at 1967 (vs), 1898 (s) and 1888 (s) cm^{-1}. On the ^{1}H-NMR spectrum, the new signals relative to the densely substituted phenol formed during the benzannulation reaction are present at 0.24, 0.31 and 1.03 ppm as singulets for the protecting group, followed by the two ethyl signals between 1.27 and 3.10 ppm and then the methoxy signal at 3.61 ppm. The other part of the spectrum is composed of signals between 4.89 and 6.15 ppm relative to the protons H1-H3 and signals between 7.56 and 8.97 ppm relative to the aromatic protons H4-H7. The new ^{13}C-NMR hydroxyarene signals of the protecting group and ethyl groups show up from -1.3 to 26.3 ppm as well as four new quaternary aromatic carbons signals between 87.3 and 140.6 ppm and of course the tricarbonylchromium signal at 233.8 ppm. The tricarbonylmanganese signal remains at 224.3 ppm. EI mass spectroscopy shows the ion-molecule's peak is present at 706.1 with an intensity of 2%.

2.4.4 X-Ray structure analysis of **17** and **18**

Crystallisation of the two complexes **17** and **18** from dichloromethane at 4°C produces in both cases dark red crystals with a monoclinic structure in a P1 21/c symmetry space group for **17** (**Figure 11**) and in a P1 21/n space group for **18** (**Figure 12**). In these complexes, the average distance between the manganese atom and the five carbon atoms of the cyclopentadienyl ring is similar to the value measured for complex **3** (all around 2.15 ± 0.01 Å) which implies that the electronic environment of the manganese moiety is not affected by the new

tricarbonylchromium phenolic ring created during the benzannulation and the diastereoisomeric position *syn* or *anti* does not matter. The average distance between the chromium atom and five carbon atoms (C4, C5, C6, C7, C7A) about 2.25 Å in complex **17** is in good agreement with Cr-C bond distances of (arene)$Cr(CO)_3$ complexes.[74] However a larger length of 2.33() Å is found for the Cr-C4A bond which indicates, as already described in the literature,[75] that the $CpMn(CO)_3$ plays an overall role similar to a donor substituent that induces a bending of the aromatic *ipso*-carbon in the opposite direction of the $Cr(CO)_3$ moiety. This kind of structure was observed in the case of tricarbonyl(2-triisopropylsilyl, 6-phenyl-anisole)chromium complex where the bulky trimethylsilyl group is anti-eclipsed with respect to a Cr-CO bond as well as in the tricarbonyl(2-methoxy-3-triisopropylsilyl, 6-phenyl-anisole)chromium complex.[76] The torsion angles α1 (C7-$Cr_{proj.}$-Cr-C121), α2 (C4A-$Cr_{proj.}$-Cr-C122) and α3 (C5-$Cr_{proj.}$-Cr-C123) are about -21.99(1)°, -22.11(1)° and -23.00(1)°, $Cr_{proj.}$ being the projection of the chromium atom on the plane of the arene (C4A, C4, C5, C6, C7 and C7A), respectively, and these data indicate an almost staggered conformation of the $Cr(CO)_3$ entity. For complex **18**, the two metallic moieties present a *syn*-orientation meaning that the sterically demanding $Mn(CO)_3$ fragment inhibits the carbon C13 to be eclipsed with respect to the $Cr(CO)_3$ tripod. Indeed, the carbon C13 is *anti*-eclipsed and carbons C4, C6 and C14 are totally eclipsed by the CO ligands. The longest Cr-C distance corresponds to the Cr-C14 bond with a 2.30(1) Å bond length in a good agreement with an overall -OTBDMS electron donating group. Furthermore, the helical twists of the two diastereoisomers are very different as shown by the measured dihedral angles. The torsion is more important in the *anti*-isomer **17** than in the *syn*-isomer **18** which can be explained by different steric pressures exerted on the polyarene by the *peri*-substitution and the metal moieties.

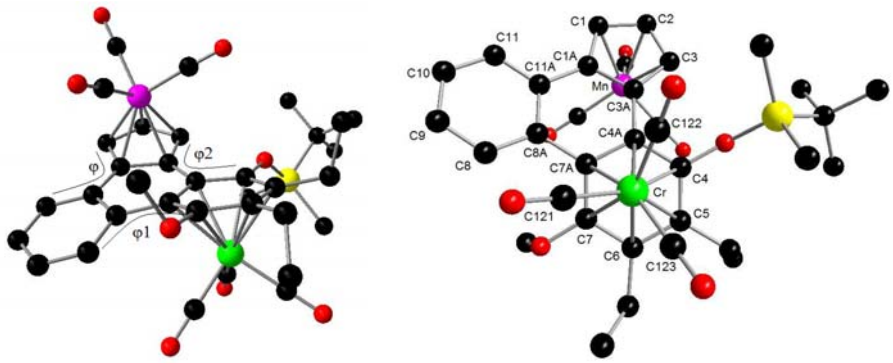


Figure 11. Molecular structure of the *anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(t*ert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese complex **17.** The numbering of atoms differs from that used in the NMR

[74] (a) V. Kunz, W. Nowacki, *Helvetica, Chim., Acta*, **1967**, *50*, 1052. (b) F. van Meurs, J. M. van der Toorn, H. van Bekkum, *J. Organomet. Chem.*, **1976**, *113*, 341, (c) F. van Meurs, H. van Koningsveld, *J. Organomet. Chem.*, **1976**, *118*, 295, (d) J. C. Boutonnet, J. Levisalles, F. Rose-Munch, E. Rose, *J. Organomet. Chem.*, **1985**, *290,* 153, (e) J. C. Boutonnet, F. Rose-Munch, E. Rose, Y. Jeannin, F. Robert, *J. Organomet. Chem.*, **1985**, *297*, 185, (f) F. Rose-Munch, E. Rose, A. Semra, M. Philoche-Levisalles, *J. Organomet. Chem.*, **1989**, *363*, 297, (g) B. Onlsson, C. Uelenius, S. Jaguer, C. Grivet, E. Wenger, E. P. Kündig, *J. Organomet. Chem.*, **1989**, *365*, 243, (h) F. Rose-Munch, K. Aniss, E. Rose, J. Vaissermann, *J. Organomet. Chem.*, **1991**, *415*, 223, (i) H.-G. Schmalz, B. Millies, J. W. Bats, G. Dürner, *Angew. Chem. Int. Ed. Engl.*, **1992**, *31*, 631, (j) F. Rose-Munch, E. Rose, J.-P. Djukic, J. Vaissermann, *Eur. J. Inorg. Chem.*, **2000**, 1295. (k) G. R. Cumming, G. Bernardinelli, E. P. Kündig, *Chem., Asian, J.*, **2006**, *1*, 459.

[75] F. Rose-Munch, E. Rose, J.-P. Djukic, J. Vaissermann, *Eur. J. Inorg. Chem.*, **2000**, 1295.

[76] J. C. Boutonnet, J. Levisalles, E. Rose, G. Precigoux, C. Courseille, N. Platzer, *J. Organomet. Chem.*, **1983**, *255*, 317.

characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C7-$Cr_{proj.}$-Cr-C121) = -21.99(1)°, α2 (C4A-$Cr_{proj.}$-Cr-C122) = -22.11(1)° and α3 (C5-$Cr_{proj.}$-Cr-C123) = -23.00(1)°. The three dihedral angles are φ (C1-C1a-C11a-C11) = -11.55(2)°, φ1 (C7-C7a-C8a-C8) = 21.87(2)° and φ2 (C3-C3a-C4a-C4) = 7.83(2)°. Selected bond lengths (Å): Mn-C1 2.15(0), Mn-C2 2.13(), Mn-C3 2.16(0), Mn-C1A 2.16(0), Mn-C3A 2.16(0), Cr-C4 2.26(), Cr-C5 2.24(1), Cr-C6 2.26(1), Cr-C7 2.24(1), Cr-C4A 2.33(), Cr-C7A 2.23(1).

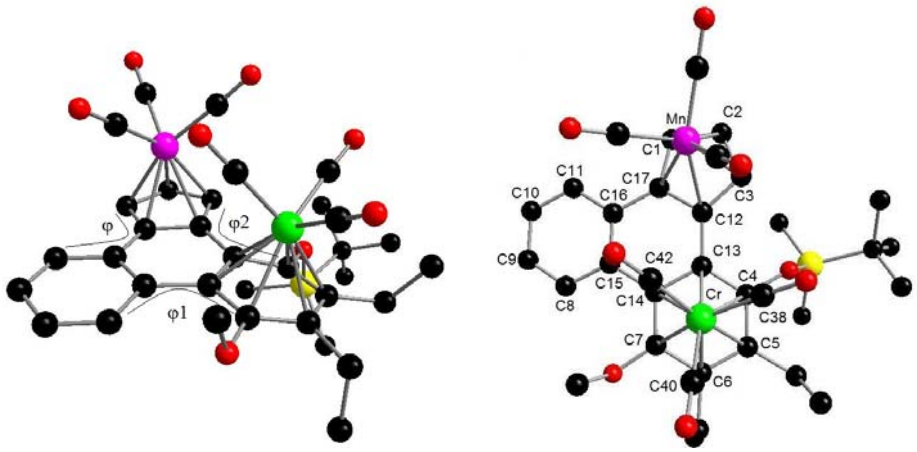


Figure 12. Molecular structure of the *syn*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese complex **18.** The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C4- $Cr_{proj.}$-Cr- C38) = -8.36(5)°, α2 (C6-$Cr_{proj.}$-Cr- C40) = -7.18(5)° and α3 (C14- $Cr_{proj.}$-Cr- C42) = -6.83(6)°. The torsion angles are φ (C1-C17-C16-C11) = -3.46(8)°, φ1 (C7 -C14-C15-C8) = -4.00(8)° and φ2 (C3-C12-C13-C4) = -9.05(9)°. Selected bond lengths (Å): Mn-C1 2.13(1), Mn-C2 2.12(2), Mn-C3 2.14(2), Mn-C12 2.24(2), Mn-C13 2.18(1), Cr-C4 2.27(1), Cr-C5 2.24(1), Cr-C6 2.20(2), Cr-C7 2.23(1), Cr-C14 2.30(1), Cr-C13 2.22(2).

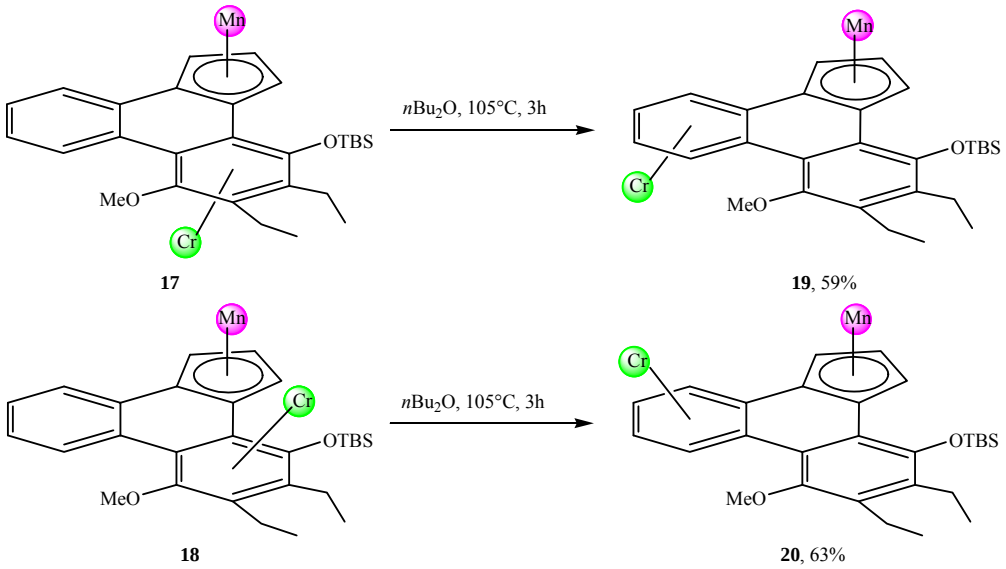
2.5 Haptotropic metal migration of complexes 17 and 18

2.5.1 Synthetic procedure

The two kinetic diastereoisomeric *syn*- and *anti*-heterobimetallic chromium-manganese complexes **17** and **18** are each dissolved in a polar and high-boiling solvent such as *n*-Bu_2O and warmed at 105°C in order to form the thermodynamic isomer complexes **19** and **20**. The reactions are followed by IR spectroscopy: the kinetic *anti*-complex **17** shows a very strong band at 1963 cm^{-1} which is transformed during the reaction at 1975 cm^{-1} corresponding to the thermodynamic *anti*-complex **19**; the kinetic *syn*-complex **18** shows a very strong band at 1967 cm^{-1} which is transformed during the reaction at 1971 cm^{-1} corresponding to the thermodynamic *syn*-complex **7**. In both cases, the reactions are complete after three hours and afford the *anti*-isomer **19** in 59% yield and the *syn*-isomer **20** in 63% yield (**Scheme 33**). In comparison with the work on densely substituted hydroquinoid phenanthrene tricarbonylchromium complexes,[77] this haptotropic migration on heterobimetallic complexes occurs equally with reasonable amounts for the *syn*- and *anti*-complexes; the reaction time is relatively short at this high temperature which leads to few decomposition. These results also mean that there is no disturbing electronic effect of the manganese which could have

[77] K. H. Dötz, J. Stendel, Jr., S. Müller, M. Nieger, S. Ketrat, M. Dolg, *Organometallics*, **2005**, *24*, 3219.

interfered during the chromium shift and there is no steric hindrance of the tricarbonylmanganese entity which could have stopped the chromium migration within the *syn*-isomer.



Scheme 33: Haptotropic metal migrations of **17** and **18**

2.5.2 Spectroscopic analysis of **19**

The IR-spectrum of **19** (in petroleum ether) indicates that the tricarbonylmanganese signals are similar to those in the starting kinetic complex **17** with two bands at 2023 (s) and 1948 (s) cm^{-1}, whereas the tricarbonylchromium signals change to give two bands at 1975 (vs) and 1913 (s) cm^{-1}. The haptotropic migration shifts the four protons H4-H7 signals from between 7.51 and 9.01 ppm in complex **17** to between 5.37 and 7.46 ppm in complex **19**. The four ^{13}C carbons signals C4-C7 are now shifted between 88.1 and 93.0 ppm. EI mass spectroscopy shows the ion-molecule's peak at 706.1 with an intensity of 4%. The peak at 622.1 (10%) represents the compound minus three carbonyl ligands, at 570.1 (11%) it shows the loss of the tricarbonylchromium, at 538.1 (14%) is the compound minus six carbonyl ligands, at 486.1 (99%) there is the loss of the chromium moiety and the three manganese's ligands and finally at 425.1 (11%) is represented the compound without any metal moiety.

2.5.3 Spectroscopic analysis of **20**

The IR-spectrum of **20** (in petroleum ether) also indicates that the tricarbonylmanganese signals are similar to those in the starting kinetic complex **18** with two bands at 2029 (s) and 1946 (m) cm^{-1}, whereas the tricarbonylchromium signals change to give two bands at 1971 (vs) and 1903 (s) cm^{-1}. The four protons H4-H7 signals are also shifted from between 7.56 and 8.97 ppm in complex **18** to between 5.58 and 7.54 ppm in complex **20**. The same effects of the haptotropic migration are observed with the four carbons signals C4-C7 now present between 87.7 and 95.7 ppm. EI mass spectroscopy shows the ion-molecule's peak at 706.1 with an intensity of 2%. The peak at 622.1 (6%) represents the compound minus three carbonyl ligands, at 570.1 (13%) it shows the loss of the tricarbonylchromium, at 538.1 (7%) is the compound minus six carbonyl ligands, at 486.2 (99%) there is the loss of the chromium moiety and the three manganese's ligands and finally at 425.1 (7%) is represented the compound without any metal moiety.

2.5.4 Comparative ^{1}H NMR analysis

Comparison between the ^{1}H NMR spectra of complexes **17** and **19** shows that the resonance of the protons H4 and H7 *ortho* to the cycle junctions are shielded by 1.55 and 1.78 ppm after the metal migration and consequently resonate at higher frequency, whereas the resonance of the protons H5 and H6 are more shielded by 2.00 and 2.14 ppm (**Table 1**, entry 1, 2 and 3). These data are in good agreement with ^{1}H NMR of other 1-,2-disubstitued (arene)tricarbonylchromium complexes such as indane derivative,[78] *N*-methyl indole,[79] and other poly-substituted complexes. Similarly, the same observations can be made comparing ^{1}H NMR spectra of complexes **18** and **20**. After the metal metallotropic rearrangement the shielding of the H5 and H6 protons are larger than those of the H4 and H7 protons which resonate at a higher frequency (**Table 1**, entry 4, 5 and 6). It is worthy to note the similar chemical shifts of the H4, H5, H6 and H7 protons of complexes **17** and **18** as well as those of complexes **19** and **20**.

Entry	Complexes and Δδ (in ppm)	H4	H5	H6	H7
1	Kinetic *anti*-complex **17**	9.01	7.60	7.51	7.83
2	Thermodynamic *anti*-complex **19**	7.46	5.60	5.37	6.05
3	$\Delta\delta$ ($\delta Hi_{\text{complex }\mathbf{17}}$-$\delta Hi_{\text{complex }\mathbf{19}}$)	1.55	2.00	2.14	1.78
4	Kinetic *syn*-complex **18**	8.96	7.61	7.58	7.80
5	Thermodynamic *syn*-complex **20**	7.54	5.75	5.58	6.35
6	$\Delta\delta$ ($\delta Hi_{\text{complex }\mathbf{18}}$-$\delta Hi_{\text{complex }\mathbf{20}}$)	1.42	1.86	2.00	1.45

Table 1. Selected ^{1}H NMR of complexes **17**, **18**, **19** and **20**. The numbering of atoms differs from that used in the X-ray analyses.

2.5.5 Comparative IR analysis

Comparison of the IR spectra of the four complexes **17**, **18**, **19** and **20** show in a general manner that the $Mn(CO)_3$ signals hardly change from one haptotropomer to the other contrary to the tricarbonylchromium signals which are different between two haptotropomers but quite similar between two diastereoisomers (**Table 2**). In the kinetic complexes **17** and **18**, the $Cr(CO)_3$ fragment is coordinated to an electron-rich tetra-substituted aromatic ring which destabilizes the metal moiety that easily migrates under thermal conditions to the non-substituted aromatic ring, leading to the thermodynamically more stable haptotropomers (**19** and **20**). In this regard, the manganese unit does not disturb the metallotropic rearrangement and its electronic environment stays unchanged, according to its IR ν(CO) bands.

Entry	Complexes	$Mn(CO)_3$	$Cr(CO)_3$	$Mn(CO)_3$	$Cr(CO)_3$	$Cr(CO)_3$
1	kinetic *anti*-**17**	2025 cm^{-1}	1963 cm^{-1}	1948 cm^{-1}	1903 cm^{-1}	1888 cm^{-1}
2	kinetic *syn*-**18**	2030 cm^{-1}	1967 cm^{-1}	1943 cm^{-1}	1898 cm^{-1}	1888 cm^{-1}
3	thermo. *anti*-**19**	2023 cm^{-1}	1975 cm^{-1}	1948 cm^{-1}	1913 cm^{-1}	-
4	thermo. *syn*-**20**	2029 cm^{-1}	1971 cm^{-1}	1946 cm^{-1}	1903 cm^{-1}	-

Table 2 : IR ν(CO) bands of complexes **17**, **18**, **19** and **20**.

[78] J. C. Boutonnet, O. Le Martret, L. Mordenti, E. Rose, G. Precigoux, *J. Organomet. Chem.*, **1981**, *221*, 147.
[79] J. C. Boutonnet, J. Levisalles, E. Rose, G. Precigoux, C. Courseille, N. Platzer, *J. Organomet. Chem.*, **1983**, *255*, 317.

2.5.6 X-Ray structure analysis of **19** and **20**.

Complexes **19** and **20** crystallize from dichloromethane at 4°C, in the monoclinic system with a lattice belonging to the symmetry space group $C\ 1_2/c$ for **19** (**Figure 13**) and in the triclinic system with a lattice belonging to the symmetry space group $P\bar{1}$ for **20** (**Figure 14**). The average distance between the manganese atom and the five carbon atoms of the cyclopentadienyl ring did not change from one haptotropomer to the other. The average distance between the chromium atom and the six carbon atoms of the phenolic ring is hardly shorter in the thermodynamic isomers than in the kinetic ones. In complex **19**, the $Cr(CO)_3$ conformation is almost staggered like in its haptotropomer **17** and the tripod is orientated outward. In complex **20**, the conformation is also staggered whereas it is eclipsed in its haptotropomer **18**, and the tripod is clearly orientated outward with the two bonds Cr-C15 and Cr-C16 (cycle-junction carbons) longer than the four others by about 0.08-0.10 Å. This was clearly shown in the case of (naphthalene)$Cr(CO)_3$[80] and (veratrole)$Cr(CO)_3$.[81] In both isomers the helical twist is as important as it is in the kinetic isomers. Probably for the same reasons as for their haptotropomers, the torsion is stronger in the thermodynamic *anti*-isomer **19** than in the thermodynamic *syn*-isomer **20** (**Table 3**).

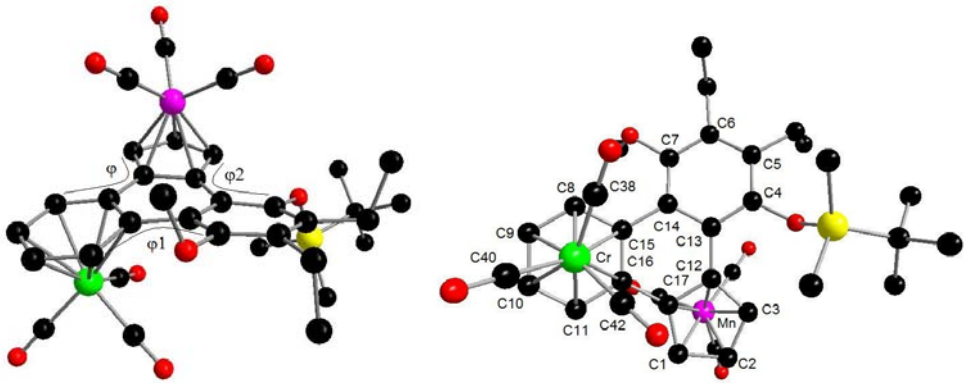


Figure 13. Molecular structure of the anti-tricarbonyl-{tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese complex **19**. The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C8-$Cr_{proj.}$-Cr-C38) = -19.32(5)°, α2 (C10-$Cr_{proj.}$-Cr-C40) = -16.28(5)° and α3 (C16-$Cr_{proj.}$-Cr-C42) = -15.87(5)°. The three torsion angles are φ (C1-C17-C16-C11) = 8.39(8)°, φ1 (C7-C14-C15-C8) = -17.31(7)° and φ2 (C3-C12-C13-C4) = -7.48(8)°. Selected bond lengths (Å): Mn-C1 2.14(1), Mn-C2 2.13(2), Mn-C3 2.13(1), Mn-C12 2.17(1), Mn-C17 2.15(1), Cr-C8 2.19(2), Cr-C9 2.21(2), Cr-C10 2.22(1), Cr-C11 2.21(1), Cr-C16 2.21(1), Cr-C15 2.26(1).

[80] V. Kunz, W. Nowacki, *Helvetica, Chim., Acta*, **1967**, *50*, 1052.
[81] J. C. Boutonnet, J. Levisalles, F. Rose-Munch, E. Rose, *J. Organomet. Chem.*, **1985**, *290,* 153.

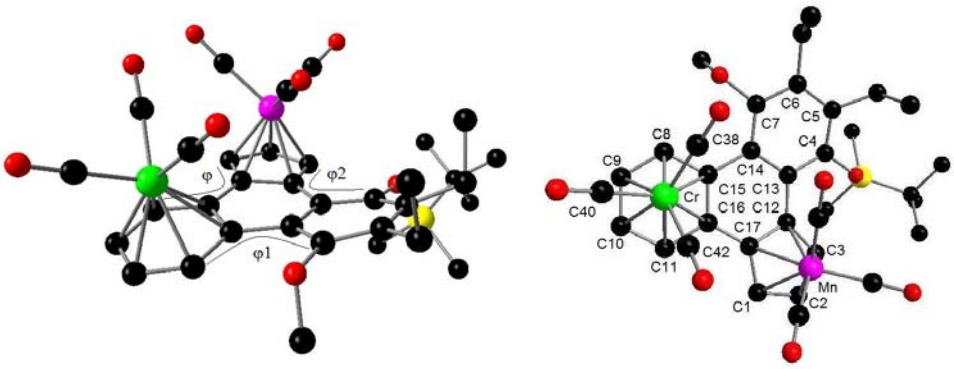


Figure 14. Molecular structure of the syn-tricarbonyl-{tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese complex **20**. The numbering of atoms differs from that used in the NMR characterization and in the name of the compound. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C15-$Cr_{proj.}$-Cr-C38) = 25.41(13)°, α2 (C9-$Cr_{proj.}$-Cr-C40) = 25.81(13)° and α3 (C11-$Cr_{proj.}$-Cr-C42) = 24.24(14)°. The three torsion angles are φ (C1-C17-C16-C11) = -0.14(21)°, φ1 (C7-C14-C15-C8) = 14.54(19)° and φ2 (C3-C12-C13-C4) = -7.05(22)°. Selected bond lengths (Å): Mn-C1 2.14(3), Mn-C2 2.13(2), Mn-C3 2.13(2), Mn-C12 2.18(3), Mn-C17 2.17(3), Cr-C8 2.20(2), Cr-C9 2.20(3), Cr-C10 2.21(3), Cr-C11 2.20(2), Cr-C16 2.29(2), Cr-C15 2.30(2).

Entry	Complexes \ Torsion angles	φ	φ1	φ2
1	kinetic *anti*-**17**	-11.55°	21.87°	7.83°
2	kinetic *syn*-**18**	3.46°	-4.00°	-9.05°
3	thermodynamic *anti*-**19**	8.39°	-17.31°	-7.48°
4	thermodynamic *syn*-**20**	0.14°	14.54°	-7.05°

Table 3 : Torsion angles between aromatic rings in complexes **17**, **18**, **19** and **20**.

2.5.7 ^{1}H-NMR kinetic study of the haptotropomerization of the *anti*-Cr-Mn complex **17**

An NMR experiment is set up in order to confirm the kinetic order of the haptotropic migration in complex **17**. Therefore hexafluorobenzene is used as solvent to guarantee this intramolecular shift (no ligand exchange possible in the liquid phase with a η^6-coordinated electron-deficient benzene bearing more than three electron-withdrawing substituents) and the reaction is performed at T= 363 K (90°C). The measurement gives a rate constant k = (3.7 ± 0.1) x 10^{-5} s^{-1} and a free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 120.3 ± 0.2 kJ.mol^{-1}. The interpretation (kinetic plots) of these results determines a first order kinetic (**Figure 15**).

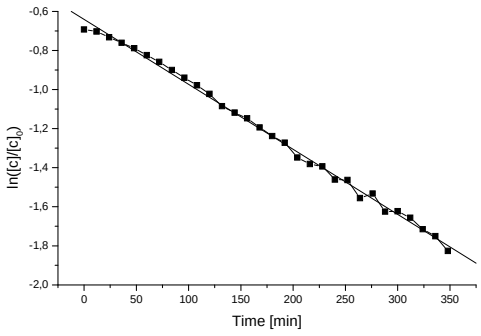
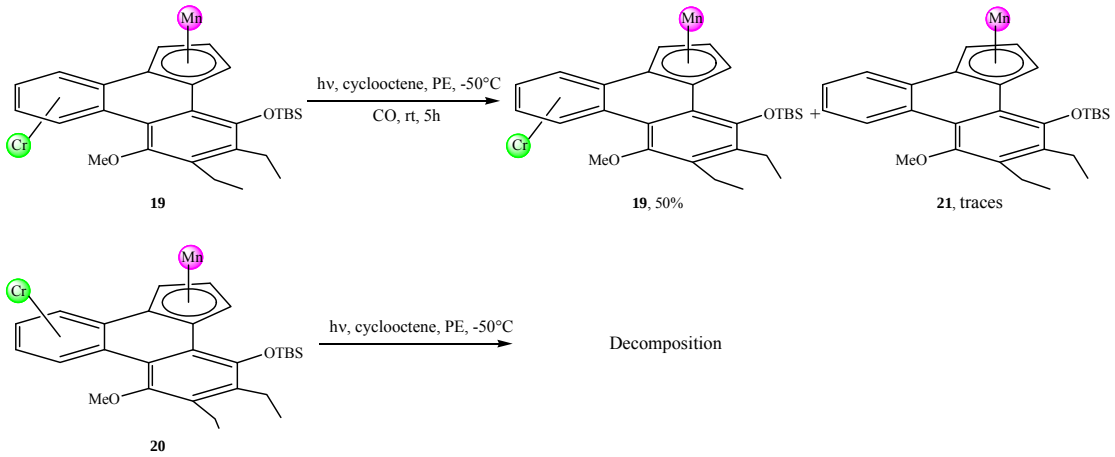


Figure 15. The linearity of the kinetic plots of the haptotropic tricarbonylchromium migration in the *anti*-Cr-Mn complex **17** at 363 K (90°C) in C_6F_6 shows a first order kinetic.

2.6 Back migration

The *anti*-Cr-Mn complex **19** and the *syn*-Cr-Mn complex **20** are both submitted to the metallotropic back-migration (**Scheme 34**). Each one is charged in a coolable shlenk made for irradiation with a gas inlet at its bottom, dissolved in a large volume of absolute petroleum ether and then cooled down to -50°C. The solution is then irradiated with a light argon flow threw it until the carbonyl ligands bands in IR spectroscopy have completely changed.
In the case of the *anti*-complex **19**, the dicarbonyl(cyclooctene)chromium complex spectrum shows three bands at 1915 (s), 1901 (s), 1871 (m) cm^{-1} and the signals of $Mn(CO)_3$ remain the same at 2021 (w) and 1944 (w) cm^{-1}. At that time, the **19** solution is allowed to reach room temperature within two hours with a carbon monoxide flow through it. As this dicarbonyl(cycloOctene)chromium complex is stable at room temperature in solution, the bubbling was prolonged until the disappearance of its signals in IR spectroscopy. The reaction is then stopped after five hours of recarbonylation. 50% of the kinetic-starting material complex **19** are isolated on a chromatographic column under argon which also purifies traces of probably a tricarbonyl(dibenz[*c*,*e*]indenyl)manganese complex **21** analysed only by MS(EI): m/z 570.2 [M^+, 11], 486.2 [M^+ -3CO, 100]. In the case of the *syn*-complex **20**, the irradiation leads directly to decomposition of the complex.



Scheme 34: Haptotropic back-migrations of **19** and **20**

2.7 Discussion/conclusion

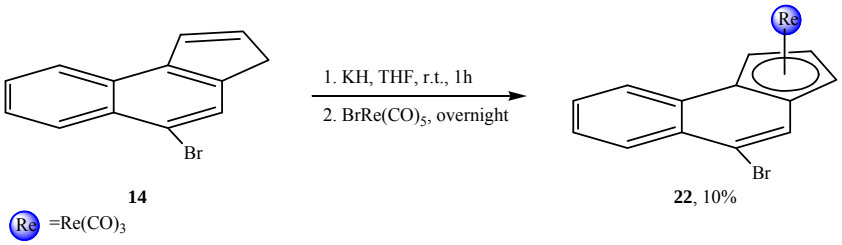
In summary, we synthesized a novel type of chromium-manganese-polyarene heterobimetallic complexes via the chromium-templated-[3+2+1] benzannulation of Fischer aryl carbenes. In these compounds, the metal moieties are bounded in a *syn*- or *anti*- arrangement with respect to the polyaromatic fused-arene ligand. Furthermore, a thermally induced haptotropic chromium migration was performed along the π-face of this polyarene system in both cases, while the manganese moiety remained identical on the Cp-ring. This cohabitation on the dibenz[*c*,*e*]indene between these two metal units extended our knowledge about the chromium migration. Suitable crystals for X-ray analyses permitted to characterize the heterobimetallic structures in the solid state. Kinetic NMR-study on the *anti*-isomer confirmed the metal shift as a first-order process.

3. Dibenzo[*c*,*e*]indene-Re-Cr system

3.1 Rhenium complexation of the 8-bromobenzo[*e*]-1*H*-indene ligand

3.1.1 Synthetic procedure

The coordination of the rhenium moiety on the 8-bromobenzo[*e*]-1*H*-indene ligand **14** has also not been reported in the literature, but our experience with manganese on that ligand will be useful. Potassium hydride is still the reactant of choice for this acid-base reaction. For the same reason as before, the use of *n*-butyl lithium is not possible because of the lithium-halide exchange side-reaction. Consequently the reaction's conditions are also really mild, the THF solution of 8-bromobenz[*e*]-1*H*-indene and potassium hydride is stirred at room temperature for one hour, followed by the addition of pentacarbonylrhenium bromide and stirred overnight at room temperature. This leads to the corresponding tricarbonylrhenium complex **22** in 10% yield (**Scheme 35**). An increased electron-richness, a greater "ring-slip" tendency and an unsymmetrical steric bulk (compared to a cyclopentadiene or an indene ligand) might be the reasons to the poor isolated yield of compound **22**.



Scheme 35: Rhenium complexation of 8-bromobenzo[*e*]-1*H*-indene **14**

3.1.2 Spectroscopic analysis of **22**

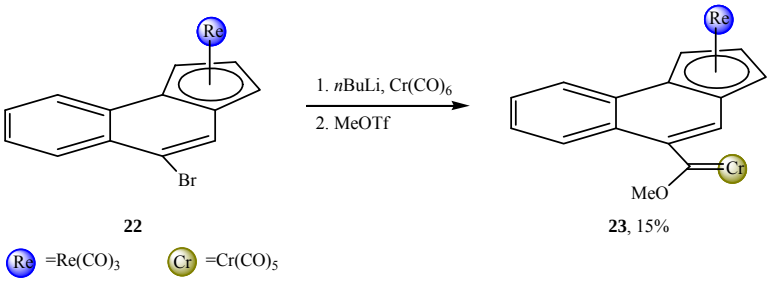
The IR-spectroscopy (in petroleum ether) shows the tricarbonylrhenium bands are present at 2027, 1936 and 1886 cm^{-1}. They are similar to those of the equivalent tricarbonylmanganese complex. The ^{1}H-NMR spectrum of **22** indicates that the tricarbonylrhenium coordination leads to three signals between 6.03 and 6.68 ppm corresponding to H1, H2 and H3 protons, with ^{3}J and ^{4}J coupling constants and in particular the ^{4}J coupling constant of 0.70 Hz between H1 and H9. The ^{13}C-NMR spectrum represents the C1, C2 and C3 signals between 72.7 and 90.0 ppm, significant of the tricarbonylrhenium complexation. The rhenium carbonyls signal is present at 193.3 ppm which is very lower than the tricarbonylmanganese signal at 224.9 ppm. Mass spectroscopy (EI) shows the ion's molecule peak at 513.9 with an intensity of 73%. The successive loss of the three carbonyls is shown by the peaks at 485.9 (40%), 457.9 (9%) and 429.9 (100%).

3.2 Fischer carbene synthesis with the tricarbonyl(8-bromobenzo[*e*]indenyl) rhenium complex 22

3.2.1 Synthetic procedure

The so-called Fischer-route is followed to synthesize a Fischer carbene with the tricarbonylrhenium complex **22**. In THF at -78°C in the presence of *n*-BuLi, the lithium-bromide exchange occurs without any nucleophilic attack on the rhenium carbonyl ligands.

The immediate addition of hexacarbonylchromium leads to the desired acyl chromate, which is then protected with methyl triflate at -50°C in DCM to afford **23** in 15% yield as an air-sensitive dark red product (**Scheme 36**).



Scheme 36: Fischer carbene synthesis with complex **22**

3.2.2 Spectroscopic analysis of **23**

The IR-spectroscopy (in petroleum ether) indicates that the three tricarbonylrhenium signals are a bit shifted at 2011 (s), 1936 (m) and 1894 (vs) cm^{-1}. Two new bands appear for the Fischer carbene carbonyls at 2067 (A1, vw) and 1971 (E, vw) cm^{-1}. It seems that the presence of the Fischer carbene modifies the rhenium moiety electronic environment because the first band is different about 16 cm^{-1} compared to complex **21**. Consequently, the interference between the Fischer carbene and this metal moiety is different than in the case of the manganese moiety where there is no modification of its bands after the chromium moiety synthesis. The three new ^{13}C-peaks corresponding to the Fischer carbene are present at 216.1, 224.8 and 356.2 ppm. Mass spectroscopy (EI) shows the ion's molecule peak at 670.0 with an intensity of 39%. The loss of carbonyls is shown by the peaks at 614.0 (10%), 586.0 (3%), 558.0 (20%) and 530.0 (100%). Dark red crystals of **23** are grown in dichloromethane at 4°C by slow evaporation. The torsion angle φ (C1-C9B-C9A-C9) = 2.84(4)° describes almost a plane in this benzo[*e*]indene ligand. The lengths of the rhenium-aromatic carbon bonds indicate that the rhenium moiety is slightly positioned in direction to carbon C2, i.e. the outside of the compound. The average distance between the metal centre and the five carbon atoms of the Cp-ring is 2.32 Å, which is 0.17 Å longer than with the tricarbonylmanganese unit. As also found in the equivalent manganese complex, the Fischer carbene - almost perpendicular to the polyaromatic plan - occupies a surprising *syn* position with respect to the $Re(CO)_3$ which is undoubtedly a consequence of the packing effect (**Figure 16**).

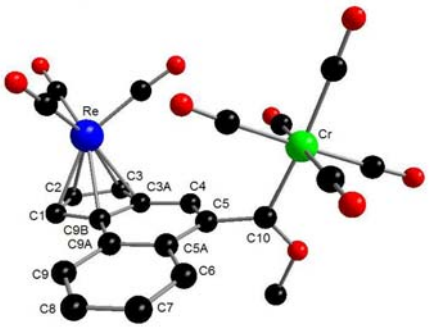
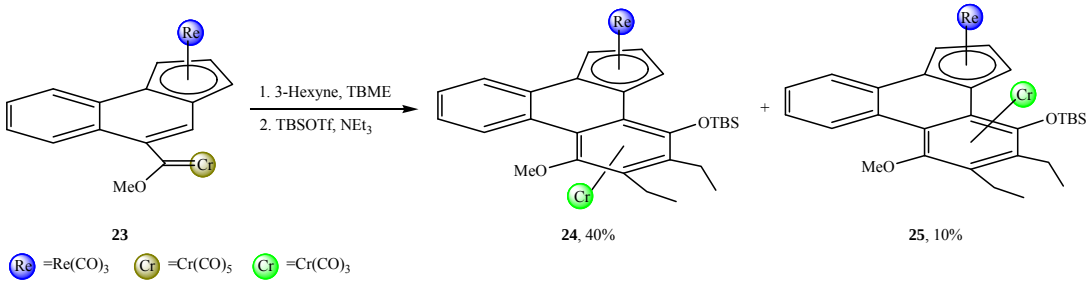


Figure 16. Molecular structure of the tricarbonyl-{pentacarbonyl[8-benzo[*e*]indenyl-(methoxy)carbene]chromium[η^5-1,2,3,3a,9a]}rhenium complex **23**. Hydrogen atoms are omitted for clarity. The dihedral angle is φ (C1-C9B-C9A-C9) = 2.84(4)°. Selected bond lengths (Å): Re-C1 2.30(1), Re-C2 2.29(1), Re-C3 2.30(1), Re-C3A 2.35(1), Re-C13 2.36(1).

3.3 Benzannulation reaction of the (Fischer carbene)-tricarbonylrhenium complex 23

3.3.1 Synthetic procedure

The two diastereoisomeric *syn* and *anti* heterobimetallic chromium-rhenium complexes are synthesized via the chromium-templated benzannulation of the Fischer aryl carbenes. The Fischer carbene **23** in the presence of 3-hexyne TBME at 60°C for two hours provides two densely substituted phenols which are subsequently protected at room temperature with a *tert*-butyl-dimethylsilyl group. After a chromatographic column, *syn*- **25** and *anti*-diastereoisomers **24** complexes are purified in 40% and 10% yield; the *anti*-isomer is the major isomer like in the precedent cases with manganese (**Scheme 37**).



Scheme 37: Chromium-templated-[3+2+1] benzannulation of complex **23**

3.3.2 Spectroscopic analysis of **24**

The IR-spectrum of **24** (in petroleum ether) shows the two rhenium bands unchanged at 2011 (s) and 1892 (vs) cm^{-1} but one signal disappeared; the tricarbonylchromium presents two bands at 1961 (w) and 1866 (sh) cm^{-1}. All the new signals relative to the new hydroquinone formed during the benzannulation reaction are present on the ^{1}H-NMR spectrum: the singulet signals at 0.44, 0.63 and 1.15 ppm corresponding to the TBDMS protecting group, followed by the two signals between 1.29 and 3.02 ppm for the two ethyl groups and of course the methoxy signal at 3.53 ppm. The other part of the spectrum is composed of signals between 5.64 and 6.74 ppm relative to the protons H1-H3, and then signals between 7.51 and 9.02 ppm relative to the aromatic protons H4-H7. Mass spectroscopy (EI) shows the ion's molecule peak at 838.1 with an intensity of 13%. At 754.1 (100%) and 702.1 (28%) are the peaks representative to the compound minus three carbonyl ligands and then minus the tricarbonylchromium moiety.

3.3.3 Spectroscopic analysis of **25**

The IR-spectrum of **25** (in petroleum ether) indicates the two rhenium bands almost unchanged at 2009 (s) and 1892 (vs) cm^{-1} but one signal disappeared. As expected the tricarbonylchromium presents two bands at 1961 (w) and 1866 (sh) cm^{-1}. The ^{1}H-NMR spectrum of **25** is similar to the spectrum of the isomer **24**. On the ^{13}C spectrum of **25**, the tricarbonylchromium signal and the tricarbonylrhenium signal are respectively at 233.7 ppm and 193.5 ppm. These two last signals have the same position as in the *anti*-isomer **24** spectrum. Mass spectroscopy (EI) shows the ion's molecule peak is present at 838.1 with an intensity of 57%. At 754.1 (100%) and 702.1 (86%) are the peaks representative to the compound minus three carbonyl ligands and then minus the tricarbonylchromium moiety.

3.3.4 X-Ray structures analysis of **24** and **25**

Crystallisation of **24** from dichloromethane at 4°C and crystallisation of **25** from diethylether at 4°C give in both cases dark red crystals. The average distance between the rhenium atom and the five carbon atoms of the Cp ring is about 2.31 and 2.33 Å in **24** and **25**, but in *syn*-**25** the Re-C3A bond is very long, over 2.41() Å, which can be explained by the close steric hindrance of the $Cr(CO)_3$ moiety. In complex **24**, The $Cr(CO)_3$ tripod is almost staggered with respect to the OTBDMS group whereas it is eclipsed in complex **25**, as indicated by the different dihedral angles α, α1 and α2 (**Figure 17** and **Figure 18**).

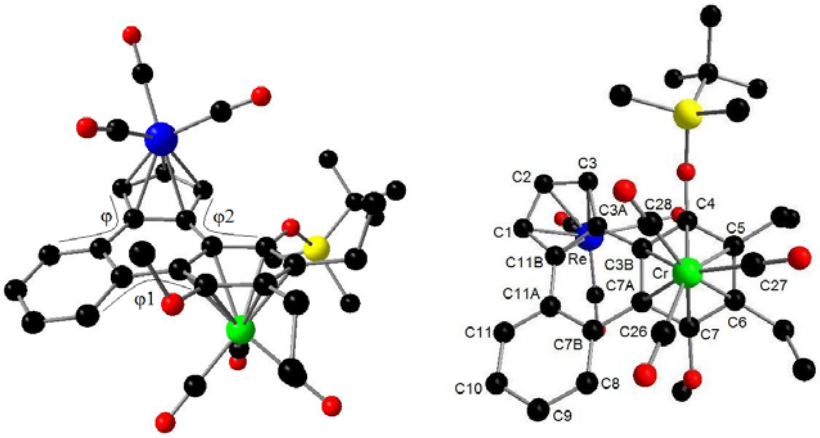


Figure 17. Molecular structure of the *anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}rhenium complex **24**. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C3B- $Cr_{proj.}$-Cr- C28) = -23.70(2)°, α2 (C5-$Cr_{proj.}$-Cr- C27) = -24.67(2)° and α3 (C7- $Cr_{proj.}$-Cr- C26) = -22.63(2)°. The three torsion angles are φ (C1-C11B-C11A-C11) = -12.10(3)°, φ1 (C7-C7A-C7B-C8) = 23.14(3)° and φ2 (C3-C3A-C3B-C4) = 6.17(3)°. Selected bond lengths (Å): Re-C1 2.31(1), Re-C2 2.30(1), Re-C3 2.29(0), Re-C3A 2.31(0), Re-C11B 2.33(0), Cr-C4 2.28(0), Cr-C5 2.24(0), Cr-C6 2.25(1), Cr-C7 2.25(1), Cr-C7A 2.23(0), Cr-C3B 2.33(1).

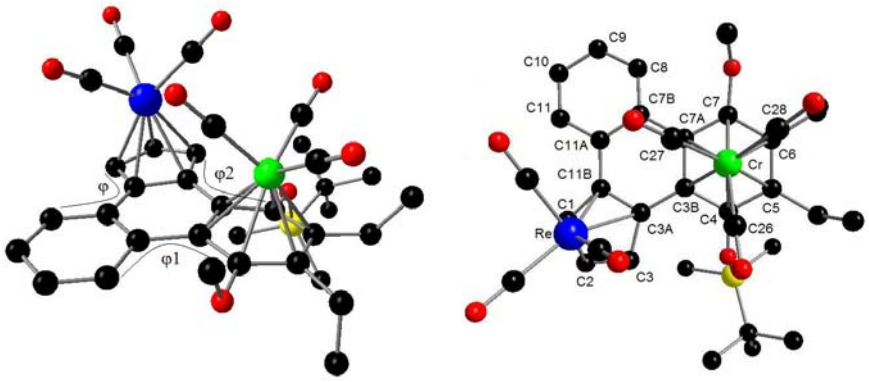
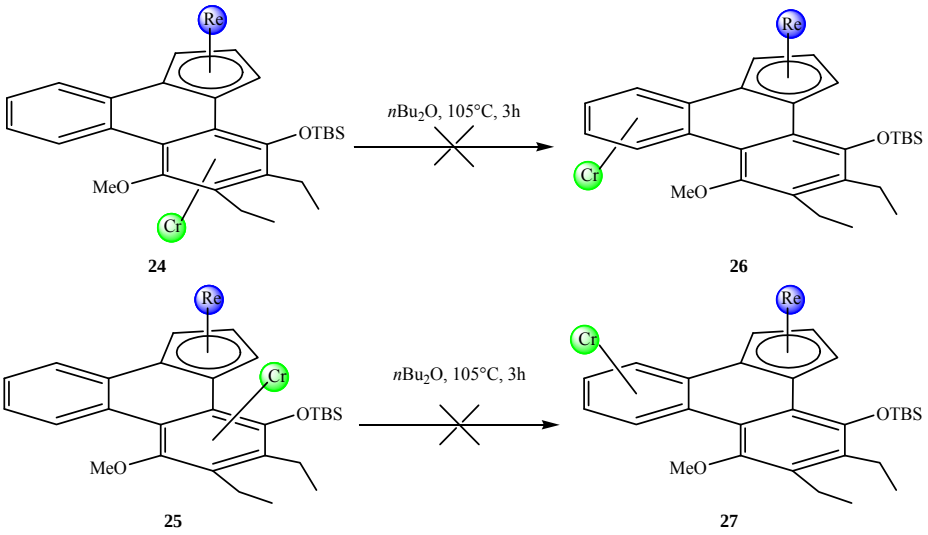


Figure 18. Molecular structure of the *syn*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}rhenium complex **25**. Hydrogen atoms are omitted for clarity. The dihedral angles are α1 (C7A- $Cr_{proj.}$-Cr- C27) = 5.87(2)°, α2 (C6-$Cr_{proj.}$-Cr- C28) = 5.54(2)° and α3 (C4- $Cr_{proj.}$-Cr- C26) = 6.48(2)°. The three torsion angles are φ (C1-C11B-C11A-C11) = 5.93(4)°, φ1 (C7-C7A-C7B-C8) = 2.71(3)° and φ2 (C3-C3A-C3B-C4) = 7.66(4)°. Selected bond lengths (Å): Re-C1 2.30(1), Re-C2 2.28(0), Re-C3 2.31(), Re-C3A 2.41(), Re-C11B 2.34(0), Cr-C4 2.27(0), Cr-C5 2.24(), Cr-C6 2.21(0), Cr-C7 2.24(1), Cr-C7A 2.30(1), Cr-C3B 2.22(0).

3.4 Haptotropic metal migration

The two kinetic diastereoisomeric *anti*- and *syn*-heterobimetallic chromium-rhenium complexes **24** and **25** were each dissolved in *n*-Bu_2O as a polar and high boiling solvent and warmed at 105°C in order to form the thermodynamic haptotropomers. In both cases, the reactions led to a decomposition of the complexes. The synthesis of complexes **26** and **27** could not be achieved (**Scheme 38**). This absence of a thermo-induced metallotropic rearrangement may be due to electronic effects. We have already noticed an interaction between the two metal moieties after the Fischer carbene synthesis of complex **23** with an important modification of the IR ν(CO) bands of the rhenium fragment, phenomenon that did not occur with the manganese unit. The $Re(CO)_3$ might redistribute the electronic environment of the fused arene and consequently disfavor the haptotropic rearrangement.



Scheme 38: Attempt of haptotropic metal migrations

2.7 Discussion/conclusion

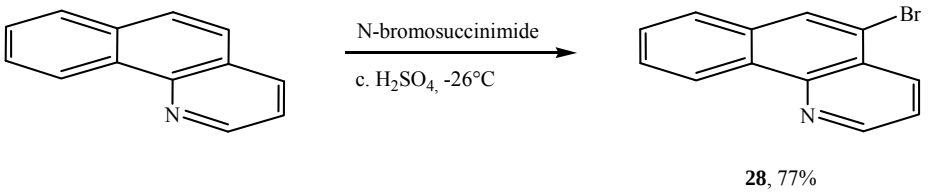
In summary, we synthesized a novel type of tricarbonylchromium-tricarbonylrhenium polyarene heterobimetallic complexes via the chromium-templated-[3+2+1] benzannulation of Fischer aryl carbenes bearing an additional rhenium label. In these binuclear compounds, the metal moieties are bounded with a *syn*-facial or *anti*-facial arrangement to the same fused-arene ligand and consequently share all the π-electrons delocalised all along the platform. Unfortunately, no thermo-induced metallotropic rearrangement was achieved. Suitable crystals for X-ray analyses were obtained to characterize all the new heterobimetallic structures.

4. Benzo[*h*]quinoline-Cr system

4.1 Synthesis of the 4-bromobenzo[*h*]quinoline 28

4.1.1 Synthetic procedure

The starting material - the 4-bromobenzo[*h*]quinoline **28** - is prepared according the procedure describing the synthesis of 5-bromoisoquinoline in 49% yield.[82] The bromination of benzo[*h*]quinoline is performed in concentrated sulphuric acid with *N*-bromosuccinimid to form an unique regioisomer - bromide in position 4 – which is purified by crystallization in petroleum ether in 77% isolated yield (**Scheme 39**).



28, 77%

Scheme 39: Synthesis of the 4-bromobenzo[*h*]quinoline **28**

4.1.2 Spectroscopic analysis of **28**

The bromination is characterized by the transformation of the doublet signal of H5 coupling with H4 in the benzo[*h*]quinoline into a singulet signal at 8.12 ppm in ligand **28**. The new quaternary carbon signal at 120.3 ppm instead of a tertiary carbon signal in the benzo[*h*]quinoline confirms the formation of the carbon-bromide bond. Neither by ^{1}H-NMR nor by ^{13}C-NMR can be determined the bromide in position 4. Further NMR analyses (2D NMR ^{1}Hx^{1}H and ^{13}Cx^{13}C) cannot enable to define the isomer. Nevertheless, the crystallizations of all the following compounds (from **29** to **35**) confirm the same and unique regioisomer.

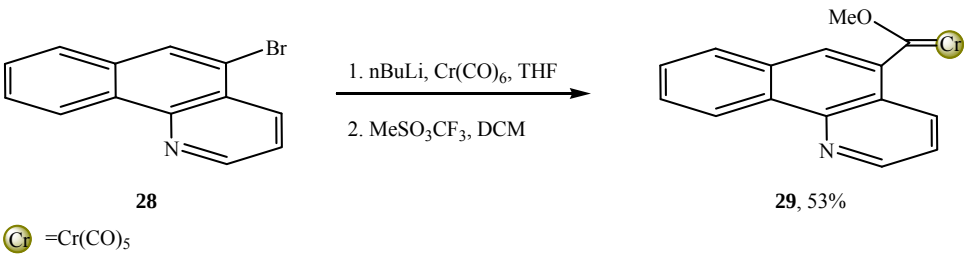
4.2 Fischer carbene synthesis with the 4-bromobenzo[*h*]quinoline 28

4.2.1 Synthetic procedure

The Fischer carbene **29** is prepared by the so-called Fischer-route. The 4-bromobenzo[*h*]quinoline **28** is dissolved in THF at -78°C and treated with *n*-BuLi, to furnish the lithiated derivative, followed by immediate addition of $Cr(CO)_6$ to lead to the desired aryl chromate, which is then alkylated by $MeSO_3CF_3$ at -50°C in CH_2Cl_2 to afford the pentacarbonyl[4-benzo[*h*]quinolyl-(methoxy)carbene]chromium(0) complex **29** in 53% yield as an air-sensitive dark red powder (**Scheme 40**). Strictly one equivalent of all the reactants is required in order to avoid any side-reactions taking place at the nitrogen: *N*-alkylation and formation of an *N*-pentacarbonylchromium complex (by a simple ligand exchange) which have already been observed on a different *N*-heterocyclic polyarene.[83] The benzo[*h*]quinoline stereoconformation might be also less favourable to form an *N*-pentacarbonylchromium

[82] W. D. Brown, A. H. Gouliaev, *Organic Synthesis*, **2005**, *81*, 98.
[83] E. Kühn, Diploma Thesis, University of Bonn, September **2006**.

complex. Indeed, for steric reasons the extended benzene ring might hamper the room next to the nitrogen atom and hinder the chromium coordination.



Scheme 40: Fischer-carbene synthesis of the 4-bromobenzo[*h*]quinoline **28**

4.2.2 Spectroscopic analysis of **29**

The IR-spectrum of **29** (in petroleum ether) shows the two characteristic Fischer carbene bands at 2065 (A1, m) and 1957 (E, vs) cm^{-1}. The two Fischer-carbene characteristic ^{13}C-peaks appear at 224.5 ppm for the carbonyl ligands and at 356.8 ppm for the carbene carbon. The methoxy group's signal shows up at 67.1 ppm. Mass spectroscopy (EI) shows the ion-molecule's peak at 413 with an intensity of 3%. The peaks at 385 (14%), 357 (7%), 329 (6%), 301 (24%) and 273 (99%) show successively the loss of the five carbonyl ligands.
Dark red crystals of **29** are obtained from dichloromethane at 4°C. The benzo[*h*]quinoline system exhibits an almost perfect planarity as evidenced by the low value of the dihedral angle φ (C9-C9a-C9b-N) = 1.57(6)°. Besides, the chromium fragment is orientated perpendicular to this polyaromatic plane as shown by the two torsion angles φ1 (Cr-C10-C4-C3a) = 91.56(5)° and φ2 (Cr-C10-C4-C5) = -86.60(5)° (**Figure 19**).

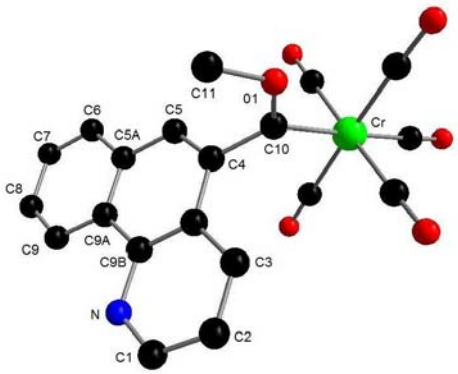


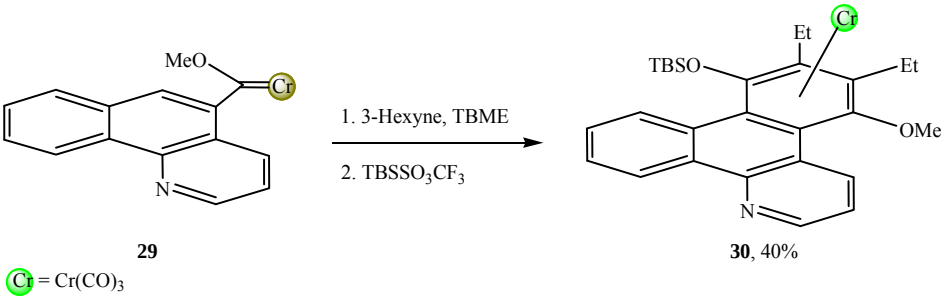
Figure 19. Molecular structure of the pentacarbonyl[4-benzo[*h*]quinolyl-(methoxy)carbene]chromium(0) complex **29.** Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Cr-C10 2.00(1), Cr-CO 1.90 ±0.01.

4.3 Benzannulation of the benzo[*h*]quinoline Fischer carbene 29

4.3.1 Synthetic procedure

The chromium-templated-[3+2+1] benzannulation procedure is followed on an *N*-heterocyclic Fischer-carbene complex **29** to form a novel tetracyclic heteroarene tricarbonylchromium complex **30**. Complex **29** is warmed in *tert*-butyl-methylether with 3-hexyne for two hours.

The new synthesized hydroxyarene is protected by addition of *tert*-butyl-dimethylsilyl triflate in the presence of triethylamine at room temperature to afford the desired tricarbonyl(dibenzo[*f,h*]quinoline)chromium complex **30** in 40% yield as an air-sensitive red powder (**Scheme 41**). This synthesis represents the first example of a benzannulation reaction on an *N*-heterocyclic-Fischer-carbene complex.



Scheme 41: Benzannulation of an *N*-heterocyclic-carbene complex **29**

4.3.2 Spectroscopic analysis of **30**

The IR-spectrum of the complex **30** shows three characteristic signals at 1961 (vs), 1903 (s) and 1886 (s) cm^{-1}. Mass spectroscopy (EI) indicates the ion-molecule's peak i at 581.2 with an intensity of 3%. The peak at 497.2 (5%) represents the complex after the loss of the three carbonyl ligands and the one at 445.2 (99%) shows the free ligand. Dark red crystals of **30** are grown from dichloromethane at 4°C. The value of the dihedral angle φ (C11-C11a-C11b-N) = 9.46(5)° slightly increases in comparison to the value in complex **29**, which indicates that the ligand establishes no longer a pseudo plane and this implies a helical twist of the compound (**Figure 20**). The chromium-hydroquinoid ring shows a slight deviation from planarity with a long Cr-C7 bond (2.30(1) Å) due to the electron donating group TBDMS, which is in good agreement with literature data.[84] The measure of the torsion angles α, α1 and α2 show an almost eclipsed conformation of the $Cr(CO)_3$ tripod with respect to the OTBDMS group.

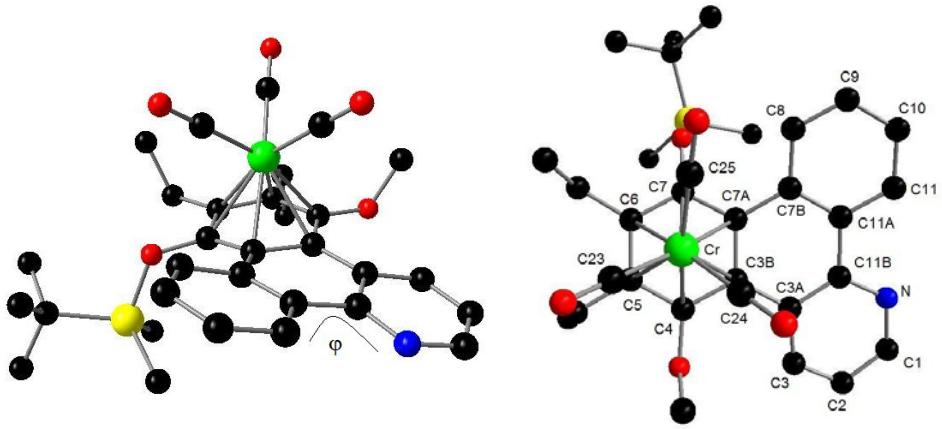


Figure 20. Molecular structure of the tricarbonyl(η^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f,h*]quinoline)chromium(0) complex **30**. Hydrogen atoms are omitted for clarity. The three torsion angles are α (C5-$Cr_{proj.}$-Cr-C23) = -5.74(4)°, α1 (C3B-$Cr_{proj.}$-Cr-C24) =

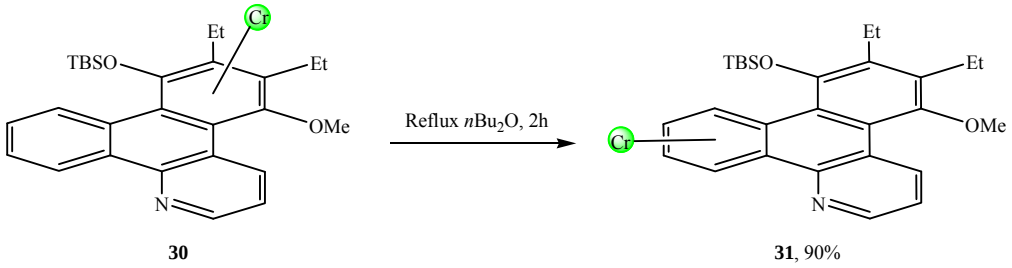
[84] F. Rose-Munch, E. Rose, J.-P. Djukic, J. Vaissermann, *Eur. J. Inorg. Chem.*, **2000**, 1295.

-5.86(4)° and α2 (C7-$Cr_{proj.}$-Cr-C25) = -7.68(4)° ($Cr_{proj.}$ is the projection of the chromium on the plane of the arene ring). Selected bond lengths (Å): Cr-C3B 2.18(1), Cr-C4 2.23(1), Cr-C5 2.21(1), Cr-C6 2.28(1), Cr-C7 2.30(1), Cr-C7A 2.21(1).

4.4 Haptotropic chromium migration of complex 30

4.4.1 Synthetic procedure

To perform the haptotropic migration of the chromium moiety along the fused-arene platform, the kinetic tricarbonylchromium complex **30** is dissolved in *n*-BuLi and warmed to 105°C in order to form the thermodynamic tricarbonylchromium complex **31**. This haptotropic metal migration is monitored by IR spectroscopy. The kinetic complex **30** shows a very strong A_1 band at 1961 cm^{-1}, which shifts progressively during the reaction to 1971 cm^{-1} characteristic for the thermodynamic stable complex **31**. After two hours the reaction is complete and a flash chromatography under argon with silica gel affords **31** in 90% yield as an air-sensitive red powder (**Scheme 42**).



30 **31**, 90%

Scheme 42: Haptotropic migration

4.4.2 Spectroscopic analysis of **31**

The IR-spectrum of **31** (in petroleum ether) indicates two main bands at 1971 (A1, vs) and 1907 (E, s) cm^{-1}; the thermodynamic complex is clearly identifiable to the kinetic one therefore one usually follows the disappearance of the A1 band at 1961 cm^{-1} in complex **30** and the formation of the A1 band at 1971 cm^{-1} in complex **31** during the migration. As confirmed by ^{1}H and ^{13}C NMR of the dibenzo[*f,h*]quinoline systems, the chromium moiety migrates to the less electron-rich benzene ring and not to the *N*-heterocyclic ring. Comparison of ^{1}H NMR spectra of **30** and **31** reveals after migration an upfield shift of 1.2-1.7 ppm for the hydrogen atoms H8-H11. There is also a slight displacement to higher frequencies of protons H1 to H3 signals which indicates that the heteroarene is slightly enriched in electrons (**Table 4**). In addition, the benzene carbon atoms C8-C11 in the ^{13}C NMR spectra are also shifted upfield by 30-40 ppm whereas the hydroquinoid carbons C4-C7 are shifted upfield by 10-15 ppm. These shifts are a very clear indication of the haptotropic chromium migration. On the other hand, ^{1}H NMR data show an unexpected and very large difference of chemical shift between the two *ortho* protons H11 and H10, $\Delta\delta = 7.44 - 5.59 = 1.85$ ppm, which is very rare for (arene)$Cr(CO)_3$ complexes.[85] Mass spectroscopy (EI) shows the ion-molecule's peak at

[85] (a) V. Kunz, W. Nowacki, *Helvetica, Chim., Acta*, **1967**, *50*, 1052; (b) F. van Meurs, J. M. van der Toorn, H. van Bekkum, *J. Organomet. Chem.*, **1976**, *113*, 341; (c) F. van Meurs, H. van Koningsveld, *J. Organomet. Chem.*, **1976**, *118*, 295; (d) J. C. Boutonnet, J. Levisalles, E. Rose, G. Precigoux, C. Courseille, N. Platzer, *J. Organomet. Chem.*, **1983**, *255*, 317; (e) J. C. Boutonnet, J. Levisalles, F. Rose-Munch, E. Rose, *J. Organomet. Chem.*, **1985**, *290,* 153; (f) J. C. Boutonnet, F. Rose-Munch, E. Rose, Y. Jeannin, F. Robert, *J. Organomet. Chem.*, **1985**, *297*, 185; (g) F. Rose-Munch, E. Rose, A. Semra, M. Philoche-Levisalles, *J. Organomet. Chem.*,

581.2 with an intensity of 8%. The peak at 497.1 (69%) represents the complex after the loss of the three carbonyl ligands and the one at 445.2 (66%) shows the free ligand.

Entry	Complexes and Δδ	H1	H2	H3	H8	H9	H10	H11
1	Kinetic complex **30**	8.64	7.52	9.15	8.79	7.33	7.30	8.67
2	Thermodynamic complex **31**	8.76	7.52	9.51	7.44	5.64	5.59	7.44
3	$\Delta\delta$ ($\delta Hi_{\text{complex }\mathbf{31}}$-$\delta Hi_{\text{complex }\mathbf{30}}$)	0.12	0.15	0.36	-1.35	-1.69	-1.71	-1.24

Table 4. Selected ^{1}H NMR of complexes **30** and **31**.

Dark red crystals of **31** are grown from dichloromethane at 4°C. There is still an increase of the dihedral angle φ (C11-C11a-C11b-N) = 14.63(2)° compared with the values in complexes **29** and then **30,** which contributes to the helical twist of the molecule. The $Cr(CO)_3$ fragment tends to turn towards the outside of the ligand just like in the case of (1,2-disubstituted-arene)$Cr(CO)_3$ complexes. The average distance between the chromium atom and the six carbon atoms of the complexed ring 2.21 Å ± 0.01 Å is only slightly shorter than in the kinetic complex **30** (**Figure 21**) and comparable to other (arene)Cr((CO)$_3$ structures.

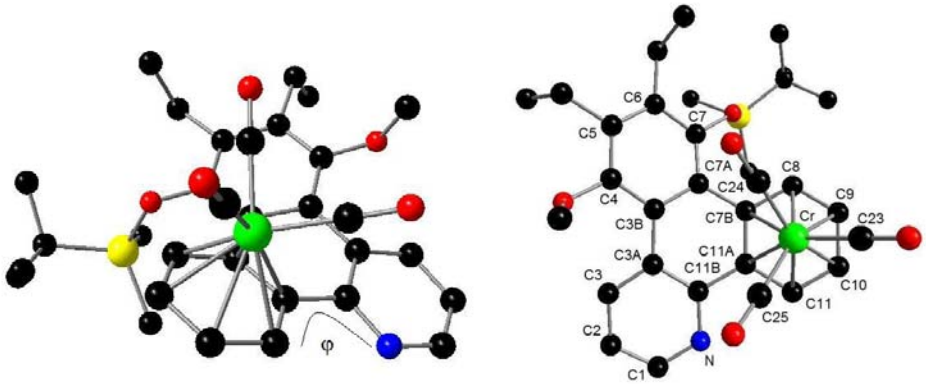


Figure 21. Molecular structure of the tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline)chromium(0) complex **31.** Hydrogen atoms are omitted for clarity. The three torsion angles are α (C9-$Cr_{proj.}$-Cr-C23) = -28.87(2)°, α1 (C7B-$Cr_{proj.}$-Cr-C24) = -32.49(2)° and α2 (C11-$Cr_{proj.}$-Cr-C25) = -26.47(2)° ($Cr_{proj.}$ is the projection of the chromium on the plane of the arene ring). Selected bond lengths (Å): Cr-C7B 2.26(0), Cr-C8 2.20(), Cr-C9 2.21(0), Cr-C10 2.22(0), Cr-C11 2.21(0), Cr-C11A 2.22(0).

4.4.3 ^{1}H-NMR kinetic study of the haptotropomerization of the $Cr(CO)_3$ complex **30**

The course of the tricarbonylchromium migration is proved to be an intramolecular process by a kinetic NMR study. Perfluorinated benzene derivates are used as solvents to guarantee this intramolecular shift. The reaction was performed at T = 353 K (80°C) in hexafluorobenzene with a DMSO-d^6 inlet as external reference. The measurement gave a rate constant k = (3.4 ± 0.1) x 10^{-3} s^{-1} and a free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 103.6 ± 0.2 kJ.mol^{-1}. The interpretation (kinetic plots) of these results shows a first order kinetic (**Figure 22**).

1989, *363*, 297; (h) B. Onlsson, C. Uelenius, S. Jaguer, C. Grivet, E. Wenger, E. P. Kündig, *J. Organomet. Chem.*, **1989**, *365*, 243; (i) F. Rose-Munch, K. Aniss, E. Rose, J. Vaissermann, *J. Organomet. Chem.*, **1991**, *415*, 223; (j) H.-G. Schmalz, B. Millies, J. W. Bats, G. Dürner, *Angew. Chem. Int. Ed. Engl.*, **1992**, *31*, 631.

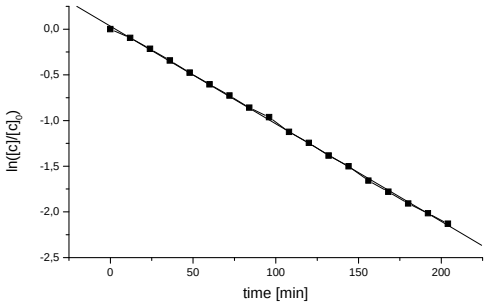
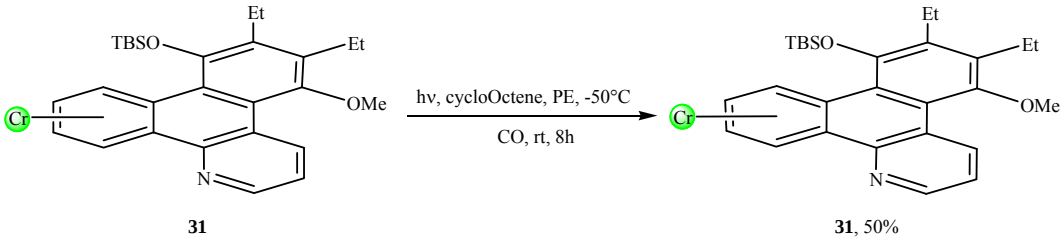


Figure 22. The linearity of the kinetic plots of the haptotropomerization of the tricarbonyl(dibenzo[*f*,*h*]quinoline)chromium complex **31** at 353 K (80°C) shows a first order process.

4.5 Back migration

The thermodynamic tricarbonyl(dibenzo[*f*,*h*]quinoline)chromium complex **31** is charged in a coolable schlenk made for irradiation with a gas inlet at its bottom, dissolved in a large volume of petroleum ether and then cooled down to -50°C. The solution is then irradiated with a light argon flow threw it until the carbonyl ligands bands in IR spectroscopy have completely changed; the dicarbonylcyclooctenechromium complex spectrum shows three bands at 1909 (s), 1901 (s), 1869 (m) cm^{-1}. At that time the solution is allowed to reach room temperature within two hours with a carbon monoxide flow through it. As this dicarbonylcyclooctenechromium complex seems to be stable at room temperature in solution, the bubbling is prolonged until the disappearance of the signals in IR spectroscopy. But after a few hours of recarbonylation, only the thermodynamic tricarbonylchromium complex is recovered. After twelve hours of bubbling, chromatography on fine silica gel with DCM affords 50% of the starting material (**Scheme 43**). There are only traces of the kinetic complex in IR spectroscopy which have not been able to be isolated.



31 **31**, 50%

Scheme 43: Back migration attempt on complex **31**

4.6 Discussion/conclusion

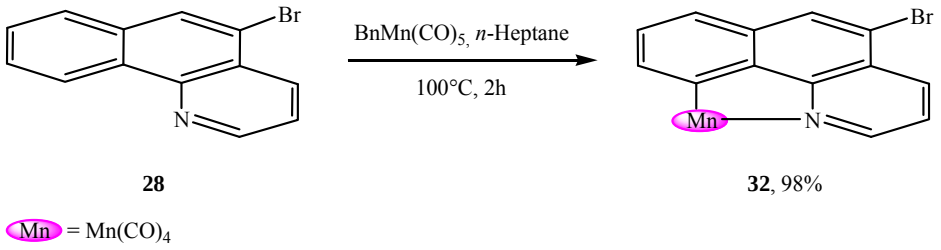
A Fischer carbene on an *N*-heterocyclic polyarene was synthesized, which was then successfully benzannulated. Subsequently, a haptotropic metal migration on this complex was performed to afford the haptotropomer in an excellent yield, which encouraged us to develop a new synthesis of heterobimetallic arene complexes in order to investigate the influence of a cyclometallated manganese moiety on the migration of a $Cr(CO)_3$ fragment along a π-platform. Kinetic NMR studies in fluorinated aromatic solvent characterized the migration as a first-order process.

5. Cyclomanganated benzo[*h*]quinoline-Cr system

5.1 Cyclomanganation of the 4-bromobenzo[*h*]quinoline 28

5.1.1 Synthetic procedure

The *ortho*-manganation of the 4-bromobenzo[*h*]quinoline **28** is synthesized via the procedure reported by Djukic *et al.*[86] using the pentacarbonyl(phenylmethane-κC^1)manganese(I) in refluxing heptane under argon for two hours. The tetracarbonyl{4-bromobenzo[*h*]quinoline-κC^9-κ*N*}manganese(I) complex **32** is produced almost quantitatively in 98% as a yellow air-stable powder (**Scheme 44**).



Scheme 44: Cyclomanganation of the 4-bromobenzo[*h*]quinoline **28**

5.1.2 Spectroscopic analysis of **32**

The four typical IR-bands at 2079 (m), 1998 (vs), 1984 (s) and 1944 (s) cm^{-1} are in good agreement with a cyclomanganated complex and correspond to the four non-equivalent carbonyl ligands. The H6 proton signal in *para* of the tetracarbonylmanganese is shifted downfield about 1.0 ppm whereas the three protons H1, H2 and H3 are shifted upfield about 0.2-0.3 ppm. On the ^{13}C-NMR spectrum, the characteristic signal of the Mn-C bond is at 171.9 ppm and the four carbonyls are present at 213.9 and 220.4 ppm. Mass spectroscopy (EI) shows the ion-molecule's peak at 422.9 with an intensity of 7%. The peaks at 338.9 (11%) and 310.9 (99%) show successively the loss of the three and four carbonyl ligands. At 256.9 (54%) is present the starting material and at 177 (20%) is the starting material less the bromide atom.
Crystallization of **32** from dichloromethane at 4°C produces yellow crystals. The *ortho*-manganated ligand represents a plane with a dihedral angle φ (C9-C9a-C9b-N) = 0.32(8)°. This hexacoordinated manganese is an octahedron with Mn-C9 and Mn-N bond-lengths of 2.06(1) and 2.07(2) Å slightly longer than the four Mn-CO bonds (**Figure 23**).

[86] J. P. Djukic, A. Maisse, M. Pfeffer, A. de Cian, J. Fischer, *Organometallics*, **1997**, *16*, 657.

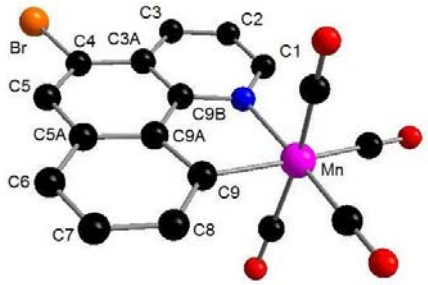
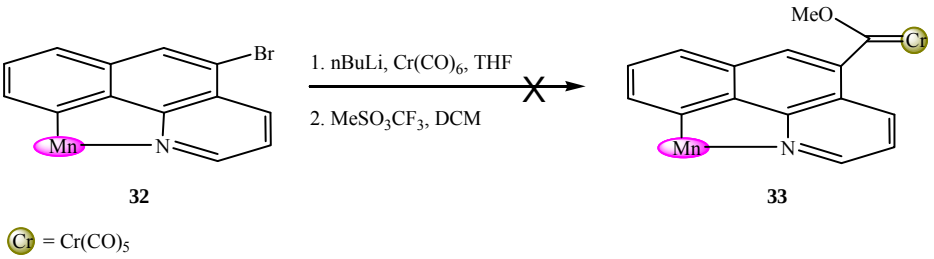


Figure 23. Molecular structure of the tetracarbonyl{4-bromobenzo[*h*]quinoline-κC^9-κN}manganese(I) complex **32**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Mn-N 2.07(1), Mn-C9 2.06(2), Mn-CO 1.835 ± 0.025.

5.2 Fischer carbene synthesis with the cyclomanganated 4-bromobenzo[*h*]quinoline complex 32

The Fischer-route type was then followed to introduce a carbene moiety onto the tetracarbonylmanganese complex **32**. But no Fischer carbene complex was formed and instead, we suggest an addition of *n*-butyl lithium on the carbonyl of the manganese which should lead to the decomposition of the manganese moiety despite the low reaction temperature (**Scheme 45**).

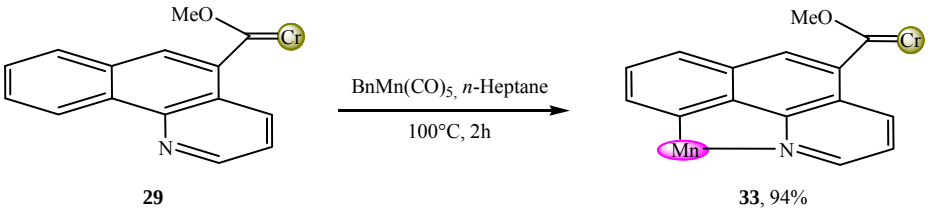


Scheme 45 : Fischer carbene synthesis on the cyclomanganated bromobenzo[*h*]quinoline **32**

5.3 Cyclomanganation of the benzo[*h*]quinoline Fischer carbene 29

5.3.1 Synthetic procedure

The reversed strategy is then applied in order to obtain the desired heterobimetallic complex **33**, which consists in the orthomanganation of the pentacarbonyl[4-benzo[*h*]quinolyl-(methoxy)carbene]chromium(0) complex **29**. The protocol used is the same as the synthesis of the tetracarbonyl{4-bromobenzo[*h*]quinoline-κC^9-κ*N*}manganese(I) complex **32**, by using the pentacarbonyl(phenylmethane-κC^1)manganese(I) complex in refluxing heptane under argon for two hours, which affords the tetracarbonyl{pentacarbonyl[benzo[*h*]quinolyl-κC^9-κ*N*-4-(methoxy)carbene]chromium(0)}manganese(I) complex **33** in 94% yield as an air-sensitive dark red powder (**Scheme 46**). It is important to observe that, despite the high reaction temperature (100°C), the Fischer carbene is stable and hardly decomposes, which can be explained by the absence of a free ligand in solution which may facilitate decomposition by loss of carbonyl ligands on the chromium.



29 **33**, 94%

Scheme 46: Orthomanganation of the Fischer-carbene complex **29**

5.3.2 Spectroscopic analysis of **33**

The IR-spectrum of **33** shows the four new peaks relative to the manganese fragment at 2079, 1996, 1984, 1943 cm^{-1}. This spectrum looks like the result of the addition of complexes **29** and **32** spectra where the two metal moieties are alone which reveals that there is no interaction between the two metal moieties. The ^{1}H-NMR spectrum shows the H6 proton signal in *para* of the $Mn(CO)_4$ shifted downfield about 1.0 ppm whereas the three protons H1, H2 and H3 are all shifted upfield about 0.22 ppm. The characteristic signal of the Mn-C bond is present at 171.9 ppm and the four carbonyls show up at 213.9 and 220.4 ppm, exactly like in compound **32**. Mass spectroscopy (EI) shows the ion-molecule's peak at 578.9 with an intensity of 8%. The peaks at 550.9 (22%), 522.9 (2%), 466.9 (38%), 438.9 (60%), 410.9 (32%), 354.9 (25%) and 326.9 (48%) show successively the loss of the nine carbonyl ligands. Crystallization from dichloromethane of **33** at 4°C produces red crystals. The small torsion angle φ (C9-C9a-C9b-N) = 0.91(1)° indicates that the benzo[*h*]quinoline in this complex also forms a plane, as found in complex **32**. The manganese moiety appears identical to what observed in complex **32**, whereas the Fischer carbene is no longer perpendicular to the aromatic plane as shown in complex **29**, which is indicated by the two torsion angles φ1 (Cr-C10-C4-C3a) = 107.28(1)° and φ2 (Cr-C10-C4-C5) = -78.06(1)° (**Figure 24**).

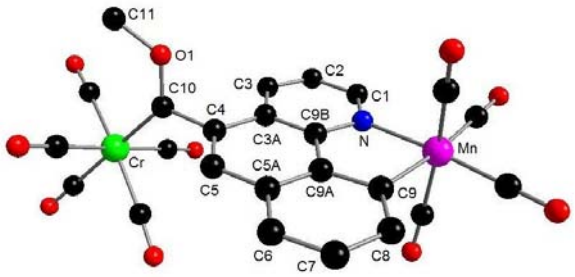


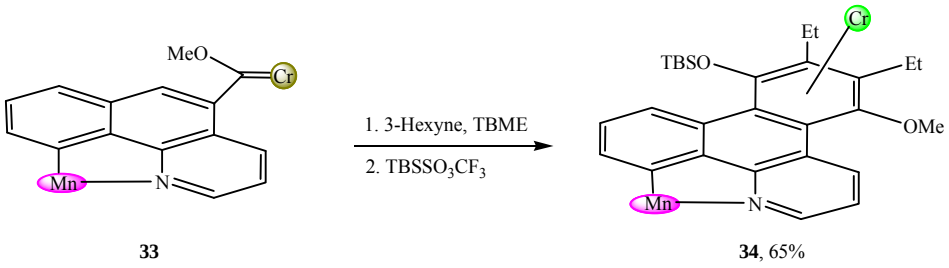
Figure 24. Molecular structure of the tetracarbonyl{pentacarbonyl[benzo[*h*]quinolyl-κC^9-κN-4-(methoxy)carbene]chromium(0)} manganese(I) complex **33**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Mn-N 2.07(), Mn-C9 2.06(0), Mn-CO 1.83 ± 0.02, Cr-C10 2.02(0), Cr-CO 1.91 ±0.01.

5.4 Benzannulation of the cyclomanganated benzo[*h*]quinoline Fischer carbene complex 33

5.4.1 Synthetic procedure

Following the usual benzannulation procedure, complex **33** is heated in *tert*-butyl-methylether in presence of 3-hexyne for two hours. The hydroxyarene is subsequently protected by

addition of *tert*-butyl-dimethylsilyl triflate in the presence of NEt_3 at room temperature to afford the heterobimetallic chromium-manganese complex **34** in 65% yield as an air-sensitive red powder (**Scheme 47**), which is better than the result of the synthesis of the non-cyclomanganated complex **30**. This result can be explained by the fact that during the benzannulation reaction, a crucial ligand exchange on chromium happens between a carbonyl and 3-hexyne while in the non-cyclomanganated complex **30**, the nitrogen electron-doublet can act as a σ-donor with respect to the chromium atom leading finally to some decomposition and thus to a lower yield.



33 **34**, 65%

Scheme 47: Benzannulation of the cyclomanganated Fischer carbene complex **33**

5.4.2 Spectroscopic analysis of **34**

The IR-spectrum of **34** shows the three new peaks corresponding to the $Cr(CO)_3$ at 1963, 1907 and 1890 cm^{-1}. It is interesting to notice that the spectrum of complex **34** looks like the virtual superposition of those of the tricarbonylchromium and the tetracarbonylmanganese complexes **30** and **32** which proves that there is no evident interaction between the two metal carbonyl groups (**Table 5**).

Complexes	$Mn(CO)_4$	$Mn(CO)_4$	$Mn(CO)_4$	$Cr(CO)_3$	$Mn(CO)_4$	$Cr(CO)_3$	$Cr(CO)_3$
30	-	-	-	1961	-	1903	1886
32	2079	1998	1984	-	1944	-	-
34	2079	1998	1984	1963	1942	1907	1890

Table 5 : IR ν(CO) bands (in cm^{-1}) of complexes **30**, **32** and **34**.

The signals relative to the new densely substituted phenol formed during the benzannulation reaction are present for -TBDMS group as singulet signals at -0.22, 0.08 and 1.18 ppm, followed by the two ethyl groups' signals between 1.40 and 3.06 ppm and the methoxy group signal at 3.76 ppm. The other part of spectrum is composed of signals between 7.49 and 9.51 ppm relative to the six aromatic protons. The carbonyl ligands' ^{13}C-NMR-signal shows up at 233.9 ppm. Mass spectroscopy (EI) shows the ion-molecule's peak at 747.2 with an intensity of 25%. The peaks at 691.2 (18%), 663.1 (6%), 635.2 (11%), 607.1 (9%), 581.2 (8%), 551.2 (27%), 497.2 (99%) and 445.2 (42%) show successively the loss of the seven carbonyl ligands, the chromium and the manganese atoms.
Crystallization from dichloromethane of **34** at 4°C produces dark red crystals. With an increasing torsion angle φ (C11-C11a-C11b-N) = 6.26(2)°, the benzo[*h*]quinoline is no longer planar. The $Cr(CO)_3$ tripod is almost eclipsed with respect to carbons C7, C5 and C3B. As already discussed with complex **30**, the formation of the hydroquinoid ring during the benzannulation induces the helical distortion which was not found in complex **34**. Nevertheless, the manganese moiety reduces this helical twist and tends, due to its octahedral

configuration, to maintain the benzo[*h*]quinoline planar (**Figure 25**). Pictures of complex **34** crystals were made during the X-Ray analyses (**Figure 26**).

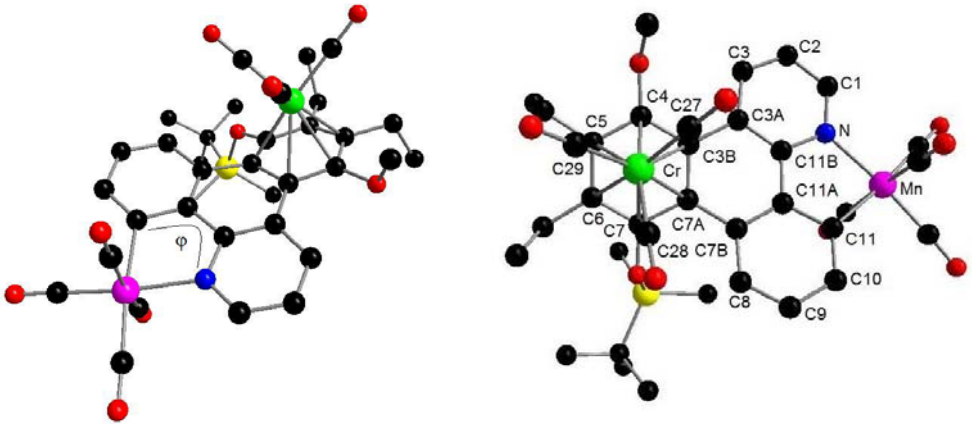


Figure 25. Molecular structure of the tetracarbonyl{tricarbonyl(η^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f,h*]quinoline-κC^{11}-κN)chromium(0)}manganese(I) complex **34.** Hydrogen atoms are omitted for clarity. The torsion angles are α (C3B-$Cr_{proj.}$-Cr-C27) = 8.12(1)°, α1 (C7-$Cr_{proj.}$-Cr-C28) = 10.38(1)° and α2 (C5-$Cr_{proj.}$-Cr-C29) = 10.50(1)° ($Cr_{proj.}$ is the projection of the chromium on the plane of the arene ring). Selected bond lengths (Å): Mn-N 2.06(0), Mn-C11 2.05(0), Cr-C3B 2.30(0), Cr-C4 2.23(0), Cr-C5 2.21(0), Cr-C6 2.29(0), Cr-C7 2.30(0), Cr-C7A 2.21(0).

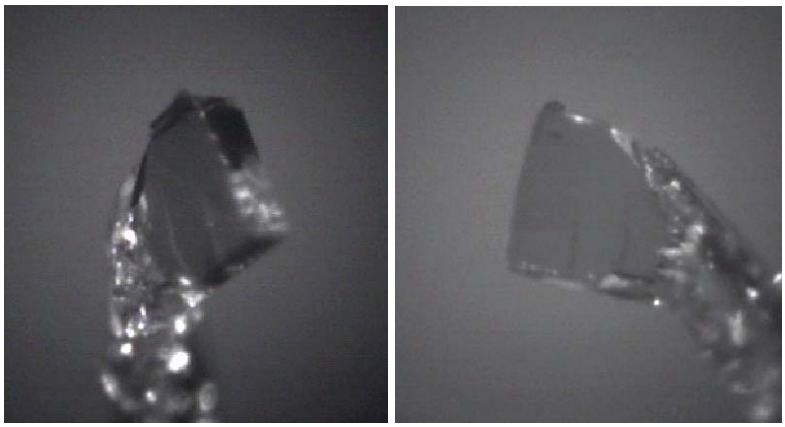


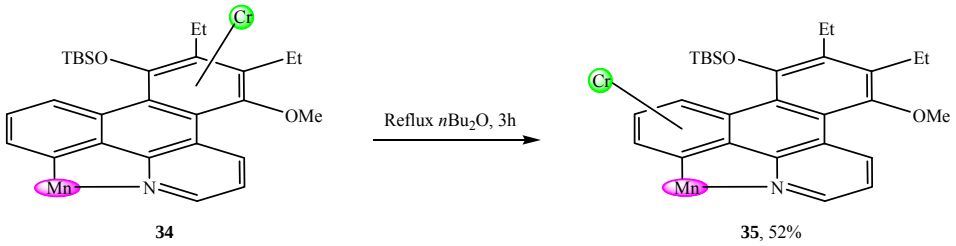
Figure 26. Pictures of complex **34** crystal structure.

5.5 Haptotropic migration of the kinetic cyclomanganated tricarbonylchromium complex 34

5.5.1 Synthetic procedure

The kinetic cyclomanganated tricarbonyl(dibenzo[*f,h*]quinoline)chromium complex **34** is then subjected to a thermo-induced haptotropic metal migration experiment and therefore warmed in nBu$_2$O to 105°C in order to form the thermodynamic stable cyclomanganated tricarbonyl(dibenzo[*f,h*]quinoline)chromium complex **35**. The reaction is monitored by IR spectroscopy. The kinetic complex **34** shows a very strong A_1 band at 1963 cm^{-1}, which shifts during the heating to 1975 cm^{-1} corresponding to the thermodynamic complex **35**. After three hours the reaction is complete and a filtration chromatography under argon affords a 52%

yield of conversion (**Scheme 48**). As expected, the tricarbonylchromium moiety migrates to the terminal benzene ring and not to the *N*-heterocyclic ring and the presence of the manganese moiety does not alter this metal rearrangement.



34 **35**, 52%

Scheme 48: Haptotropic metal migration on the cyclomanganated tricarbonyl(dibenzo[*f,h*]quinoline)chromium

5.5.2 Spectroscopic analysis of **35**

The IR spectrum of complex **35** shows a weak interaction between the two metal moieties with the tricarbonylchromium wavelengths being 5-8 cm^{-1} longer than the values given by the IR spectrum of complex **31** (**Table 6**). The manganese moiety on the ligand behaves as an electron donor and the chromium moiety as an electron acceptor.

Complexes	$Mn(CO)_4$	$Mn(CO)_4$	$Mn(CO)_4$	$Cr(CO)_3$	$Mn(CO)_4$	$Cr(CO)_3$
31	-	-	-	1971	-	1907
32	2079	1998	1984	-	1944	-
35	2085	2006	1988	1975	1950	1898

Table 6 : IR wave bands (in cm^{-1}) of complexes **31**, **32** and **35**.

The ^1H NMR spectra of **34** and **35** reveal an upfield shift of 1.2-2.1 ppm for the hydrogen atoms H8-H10 (**Table 7**); the benzene-carbon atoms C8-C10 in the ^{13}C NMR spectra are also shifted upfield by 30-38 ppm whereas the hydroquinoid carbons C4-C7 are shifted upfield by 8-13 ppm. These shifts are typical for the haptotropic chromium rearrangement. In mass spectroscopy (EI), the ion-molecule's peak is present at 747.1 with an intensity of 1%. The peaks at 663.1 (29%), 635.1 (36%), 607.1 (26%), 551.1 (2%), 497.2 (99%) and 445.3 (14%) show successively the loss of the carbonyl ligands, the chromium and the manganese atoms.

Entry	Complexes and Δδ	H1	H2	H3	H8	H9	H10
4	complex **34**	9.50	7.50	9.03	8.12	7.55	8.68
5	complex **35**	9.63	7.50	8.84	6.23	5.46	7.44
6	$\Delta\delta$ ($\delta Hi_{complex\ 35}$-$\delta Hi_{complex\ 34}$)	0.13	0.00	-0.19	-1.89	-2.09	-1.24

Table 7. Selected ^1H NMR of complexes **34** and **35**.

Crystallization from dichloromethane of **35** at 4°C results in dark red crystals with a triclinic structure from the space group $P\bar{1}$. The haptotropic migration slightly intensifies the helical torsion as shown by the dihedral angle φ (C11-C11a-C11b-N) = -8.93(4)°, which is however less prominent than in the non-manganated thermodynamic system. The $Cr(CO)_3$ tripod is almost staggered due to the hindrance of the Mn moiety and consequently the sterical interactions between the different CO ligands. Furthermore, the Cr-C11 bond is the longest

Cr-C bond which indicates that the $Mn(CO)_3$ acts like an electron-donating substituent which moves away the carbon C11 from the chromium fragment (**Figure 27**).
In solution, ^{1}H NMR data of the H8, H9 and H10 aromatic protons are unusual. Indeed, they resonate respectively at 6.23, 5.46 and 7.44 ppm. As encountered with complex **31**, $\Delta\delta = \delta_{H10}$-$\delta_{H9}$ = 2.02 ppm represents the largest difference of chemical shift to our knowledge between two adjacent protons in (arene)$Cr(CO)_3$ complexes, probably due to the constraint conformation of the chromium moiety and intensified by the carbonyl C29O9 of the $Mn(CO)_4$ entity.

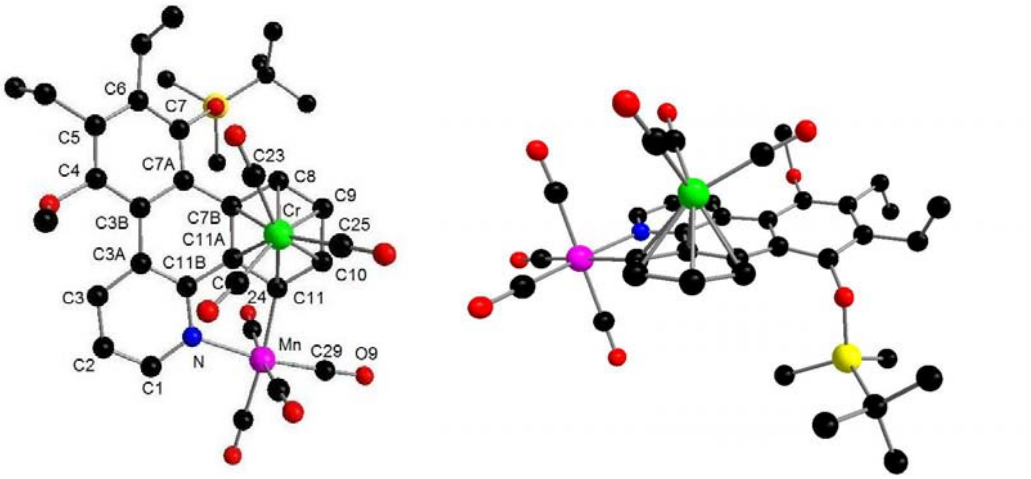


Figure 27. Molecular structure of the tetracarbonyl{tricarbonyl(η^6-7b,8,9,10,11,11a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline-κC^{11}-κN)chromium(0)}manganese(I) complex **35**. Hydrogen atoms are omitted for clarity. The torsion angles are α (C8-$Cr_{proj.}$-Cr-C23) = 24.59(3)°, α1 (C11A-$Cr_{proj.}$-Cr-C24) = 18.88(4)° and α2 (C10-$Cr_{proj.}$-Cr-C25) = 22.28(4)° ($Cr_{proj.}$ is the projection of the chromium on the plane of the arene ring). Selected bond lengths (Å): Mn-N 2.07(1), Mn-C11 2.05(1), Cr-C7B 2.34(1), Cr-C8 2.21(1), Cr-C9 2.22(1), Cr-C10 2.28(1), Cr-C11 2.34(1), Cr-C11A 2.20(1).

5.5.3 ^{1}H-NMR kinetic study of the haptotropomerization of the Cr-Mn complex **34**

A kinetic NMR study in C_6F_6 was carried out to prove the intramolecular character of this reaction and to compare it with the metal migration in the non-cyclomanganated complex **30**. The measurement performed at T= 353 K (80°C) gives a rate constant $k = (10.7 \pm 0.1) \times 10^{-3}$ s^{-1} and a free activation enthalpie for the transition state $\Delta G^{\ddagger} = 100.3 \pm 0.2$ kJ.mol^{-1}. The graphical plots reveal first order kinetics (**Figure 28**). The rate constants obtained in both kinetic-NMR experiments demonstrate that the chromium migration was about three times faster in the cyclomanganated complex **34** than in the non-cyclomanganated complex **30**. The free activation enthalpy for the transition state was lower in this heterobimetallic complex **34**. Consequently, on one hand the manganese fragment favoured the haptotropic rearrangement but on the other hand decreased slightly the yield, which might be caused by a partial decomplexation of the heterobimetallic complex during the process.

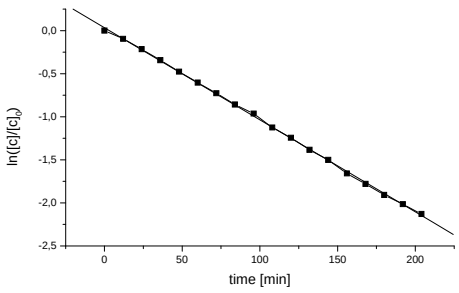
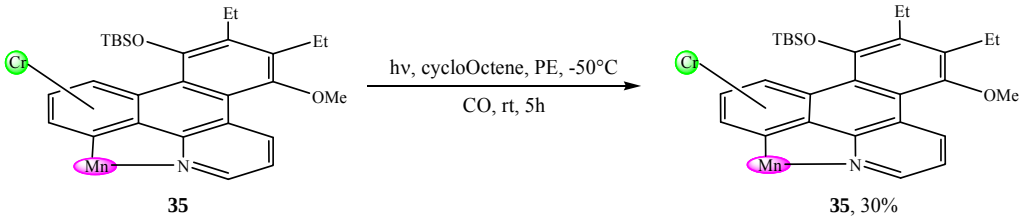


Figure 28. The linearity of the kinetic plots of the haptotropic migration of the cyclomanganated (dibenzo[*f*,*h*]quinoline)Cr(CO)$_3$ complex **35** at 353 K (80°C) shows a first order process.

5.6 Back migration

The cyclomanganated tricarbonyl(dibenzo[*f,h*]quinoline)chromium complex **35** is charged in a coolable schlenk made for irradiation with a gas inlet at its bottom, dissolved in a large volume of petroleum ether and then cooled down to -50°C. The solution is then irradiated with a light argon flow threw it until the carbonyl ligands bands in IR spectroscopy have completely changed; the spectrum of the dicarbonylcyclooctenechromium complex shows three bands at 1905 (s), 1889 (s) and 1846 (m) cm^{-1}. At that time the solution is allowed to reach room temperature within two hours with a carbon monoxide flow through it. As this dicarbonylcyclooctenechromium complex seems to be stable at room temperature in solution, the bubbling is prolonged until the disappearance of its signals in IR spectroscopy. But after a few hours of recarbonylation, only the thermodynamic tricarbonylchromium complex is recovered. After twelve hours of bubbling, chromatography on fine silica gel with DCM affords 30% of the starting material **35** (**Scheme 49**). There are no traces of the kinetic complex in IR spectroscopy.



Scheme 49: Attempt of a haptotropic back-migration on complex **35**

5.7 Discussion/conclusion

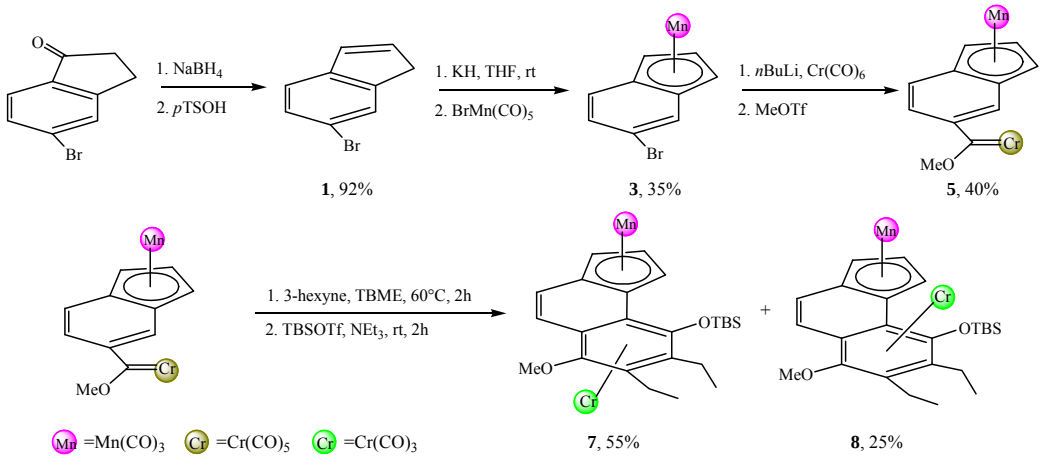
The introduction of the tetracarbonylmanganese fragment takes place between the Fischer-carbene synthesis and the benzannulation reaction, affording the desired *N*-heterocyclic-polyarene heterobimetallic complex. The haptotropic metal rearrangement is achieved by a thermal induction to produce the isomer with chromium coordinated to the terminal benzene ring of the polyarene. Kinetic NMR studies in fluorinated aromatic solvent characterized the migration as a first-order process in both cases. The manganese fragment lowered the free activation enthalpy for the transition state and increased the migration rate by a factor of 3 but also slightly reduced the chemical yield.

IV] CONCLUSION AND OUTLOOK

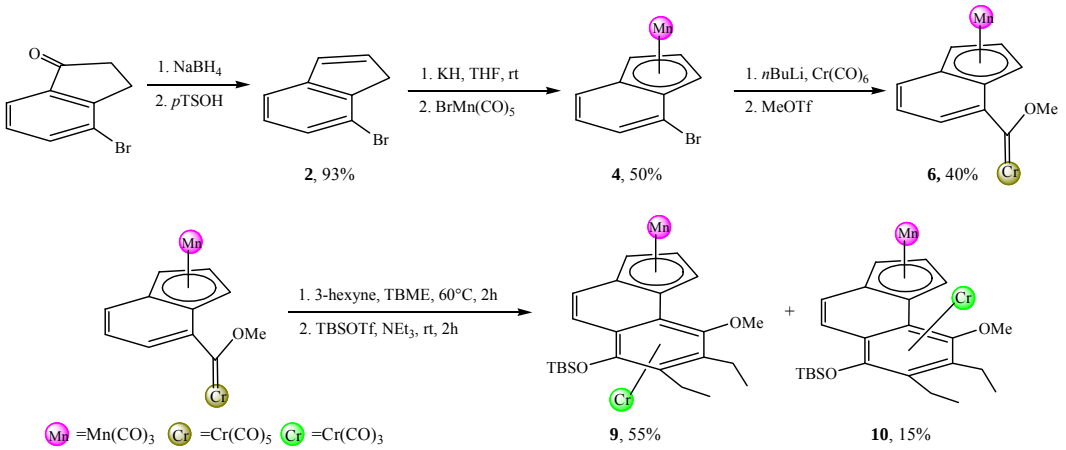
A characteristic property of transition metal π-complexes with polycyclic aromatic ligands is their ability to undergo haptotropic rearrangements; the metal fragment is considered as the moveable functional group that is shifted between two non-equivalent rings of an oligocyclic ligand.
We decided to add a second metal unit coordinated to the arene skeleton in order to study its influence on the migration of the chromium moiety. In this context, we synthesized the first heterobimetallic $Cr(CO)_3$-$Mn(CO)_3$ and $Cr(CO)_3$-$Re(CO)_3$ oligocyclic fused arene complexes. We also explored a novel synthesis of cyclomanganated *N*-heterocyclic polyarene-$Cr(CO)_3$ complexes. In all cases, the chromium-templated-[3+2+1] benzannulation was employed to introduce the chromium moiety.

1. Heterobimetallic benzo[*e*]indene $Cr(CO)_3$-$Mn(CO)_3$ complexes

The first bimetallic complexes were synthesized by the following strategy: The benzannulation of Fischer arylcarbenes bearing an additional metal label afforded the desired heterobimetallic complexes. The synthesis of these heterobimetallic complexes started first with the 5-bromoindene (**Scheme 50**) and 4-bromoindene (**Scheme 51**) ligands to validate our strategy. A novel synthesis of the $Mn(CO)_3$-complexes **3** and **4** was followed by the formation of Fischer carbenes **5** and **6** by their chromium-templated benzannulation; this reaction provided angular *anti*- **7** and **9** and *syn*- **8** and **10** diastereomers of the heterobimetallic $Cr(CO)_3$-$Mn(CO)_3$ complexes. Neither in IR and NMR spectroscopies or in X-Ray analyses was observed a cooperation or interaction between the two metal units. In a general manner, It also seems that the permutation between the *peri*-substitution (-Me and -TBS) does not affect the crystal structures of the complexes (we need the crystal structure of complex **10** to confirm this observation).



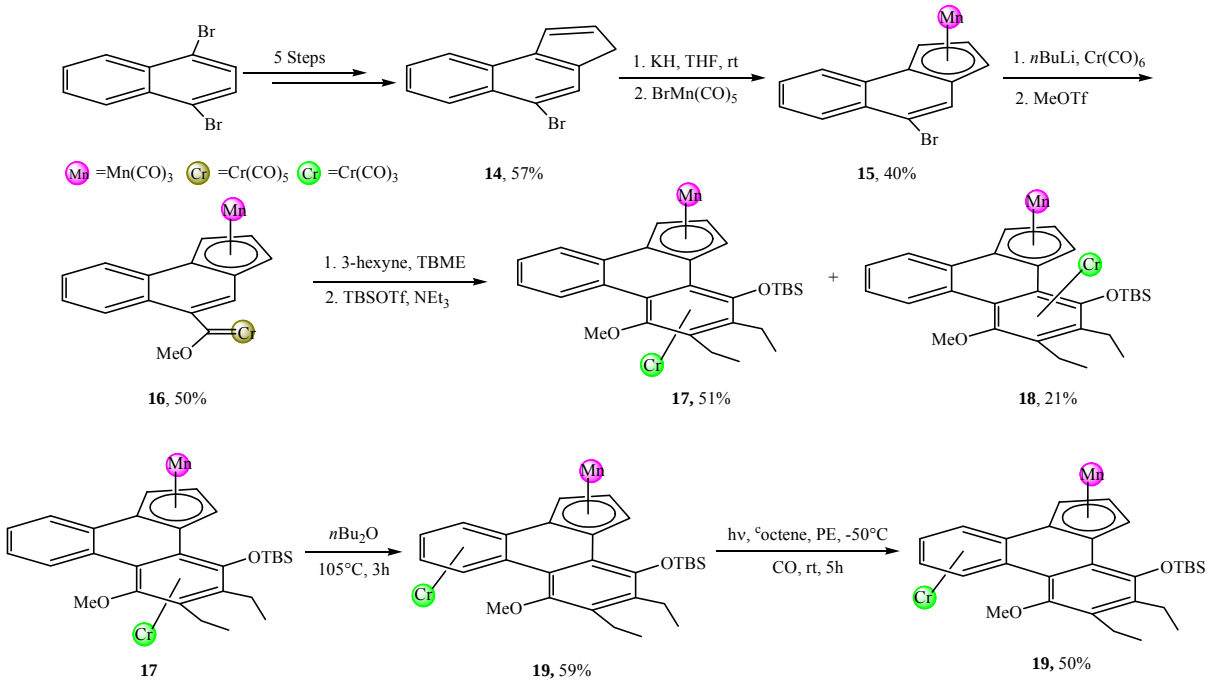
Scheme 50: From 5-bromo-1-indanone to heterobimetallic benzo[*e*]indene $Cr(CO)_3$-$Mn(CO)_3$ complexes **7** and **8**

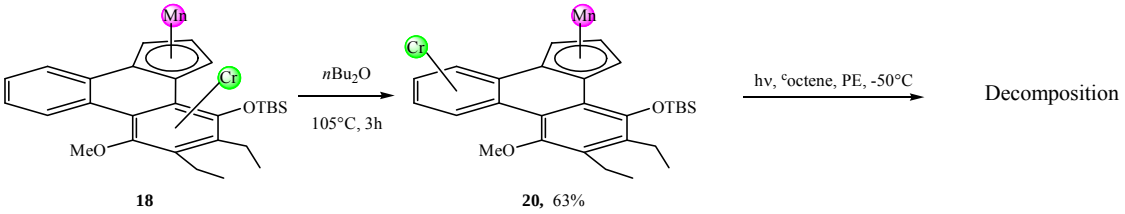


Scheme 51: From 4-bromo-1-indanone to heterobimetallic benzo[*e*]indene $Cr(CO)_3$-$Mn(CO)_3$ complexes **9** and **10**

2. Heterobimetallic dibenzo[*c*,*e*]indene $Cr(CO)_3$-$Mn(CO)_3$ and $Cr(CO)_3$-$Re(CO)_3$ complexes

These first successful results on the heterobimetallic benzo[*e*]indene-$Cr(CO)_3$-$Mn(CO)_3$ complexes encouraged us to develop a platform with an extended aromatic ring which would allow a metallotropic rearrangement. Thus we started from the 1,4-dibromonaphthalene to synthesize the 8-bromobenzo[*e*]-1*H*-indene **14** in 57% yield over a five-step sequence. We then followed the same strategy as previously to obtain our desired binuclear complexes **17** and **18**. In the case of the $Cr(CO)_3$-$Mn(CO)_3$ system, the thermally induced haptotropic metal migration produced in 60% yield the two haptotropomers **19** and **20**. The attempt to make a molecular switch feasible via a light-induced back migration failed and yielded either to the starting material or to decomposition (**Scheme 52**).

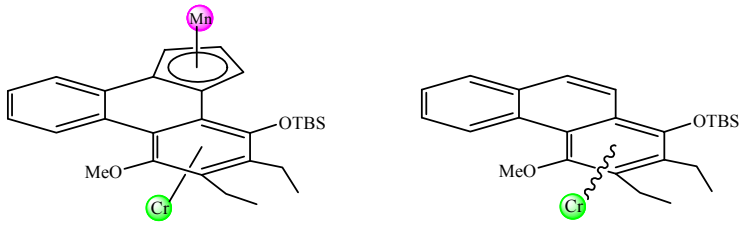




18 **20,** 63%

Scheme 52: From 1,4-dibromonaphthalene to heterobimetallic dibenzo[*c*,*e*]indene-$Cr(CO)_3$-$Mn(CO)_3$ complexes **17**, **18**, **19** and **20**

The intramolecular course of the chromium fragment was confirmed with the *anti*-isomers **17** by NMR studies that shows first order kinetic. The interpretation of the NMR kinetic studies of the haptotropomerization of the *anti*-Cr-Mn complex **17** and of the equivalent simpler phenanthrene system **36**[87] shows clearly that the introduction of the cymanthrene fragment considerably increased the free activation state and dramatically lowered the rate of the migration by a factor of 43 (**Figure 29**). Thus, this second metal unit disfavoured but did not prevent the metallotropic rearrangement.

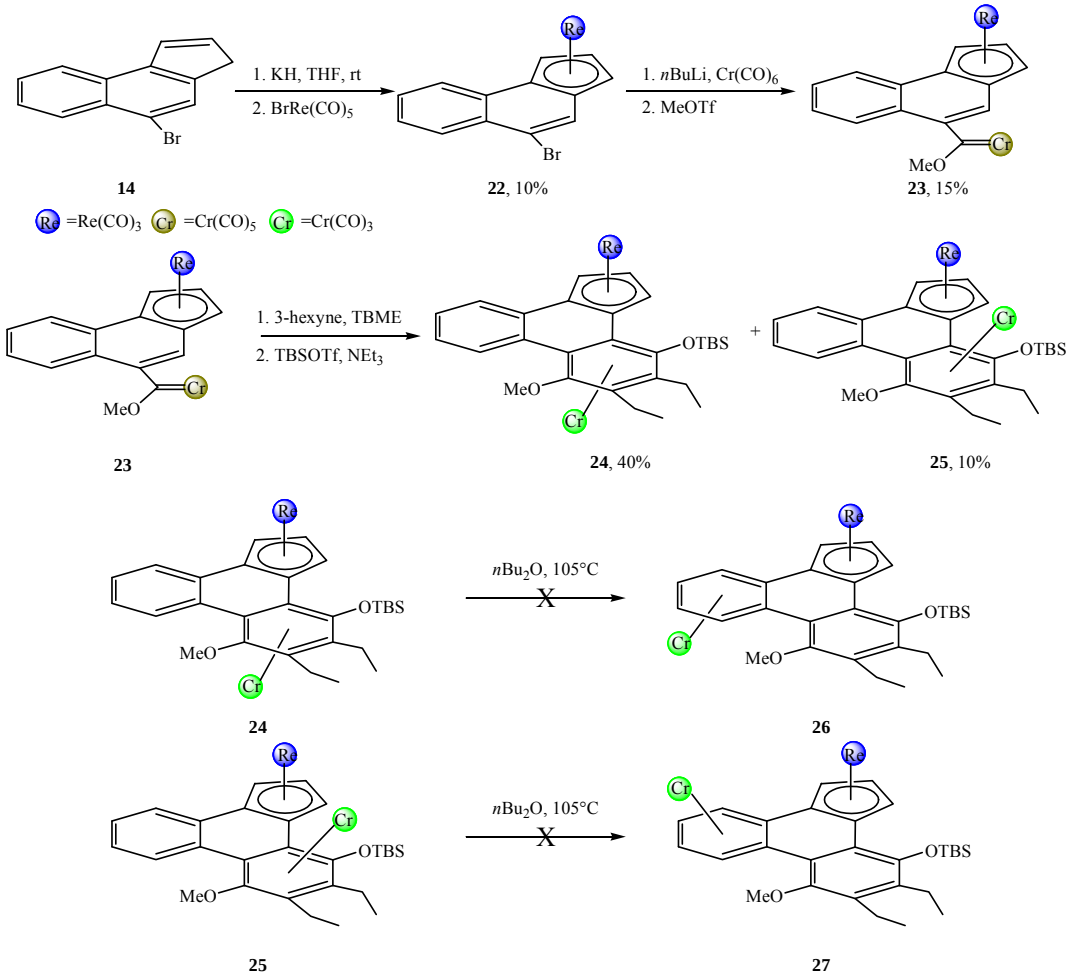


17 **36**

Figure 29: Comparison of NMR kinetic studies for **17**: rate constant k = (3.7 ± 0.1) x 10^{-5} s^{-1}, free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 120.3 ± 0.2 kJ.mol^{-1} and **36**: rate constant k = (1.6 ± 0.2) x 10^{-3} s^{-1}, free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 104.3 ± 0.3 kJ.mol^{-1}.

We then decided to extend our system to other metal and chose the rhenium transition metal which is in the same column as the manganese atom and coordinate the same way to Cp-ligands. We used successfully the same procedure to furnish to our knowledge the first heterobimetallic complexes **24** and **25**. Unfortunately no haptotropic metal migration occurred with the $Cr(CO)_3$-$Re(CO)_3$ system (**Scheme 53**).

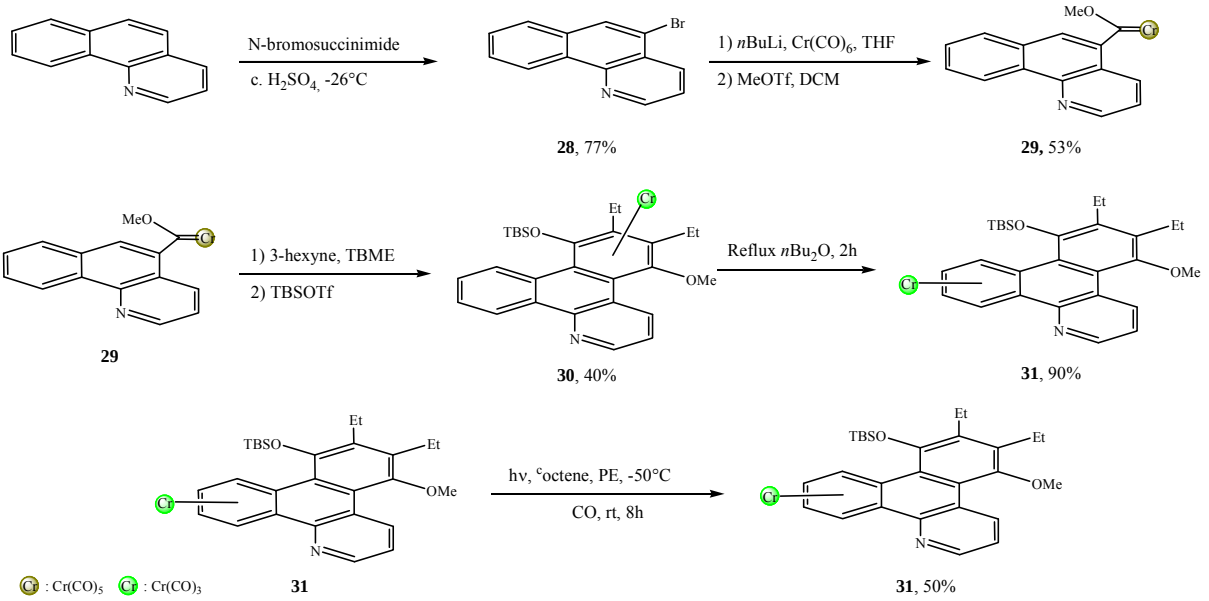
[87] K. H. Dötz, J. Stendel, Jr., S. Müller, M. Nieger, S. Ketrat, M. Dolg, *Organometallics*, **2005**, 24, 3219.



Scheme 53 : From 1,4-dibromonaphthalene to heterobimetallic dibenzo[*c*,*e*]indene-$Cr(CO)_3$-$Re(CO)_3$ complexes **24** and **25**

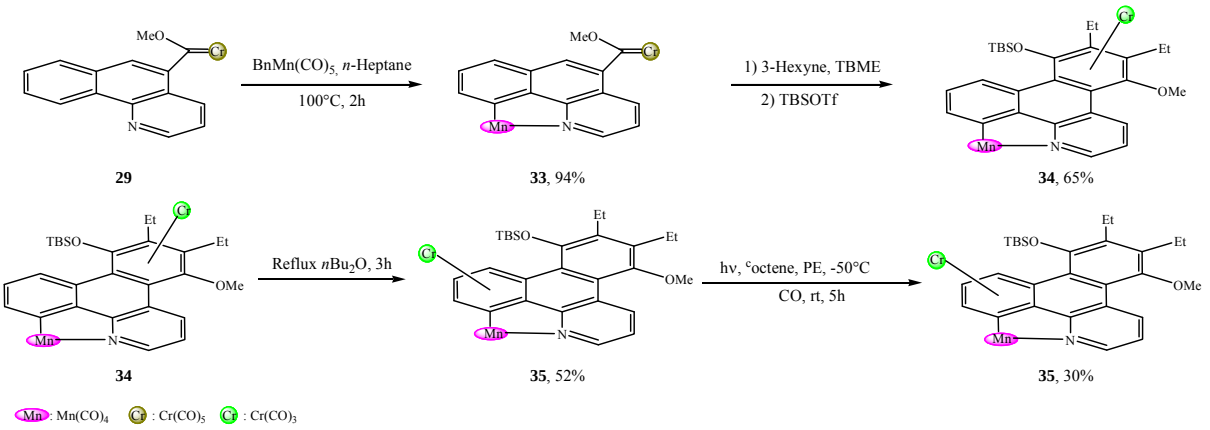
3. (η^6-*N*-heterocyclic-polyarene)$Cr(CO)_3$ and cyclomanganated (η^6-*N*-heterocyclic-polyarene)$Cr(CO)_3$ complexes

A Fischer carbene on an *N*-heterocyclic polyarene was also synthesized, which was then successfully benzannulated (**Scheme 54**). Subsequently, a haptotropic metal migration on this complex was performed to afford the haptotropomer **31** in an excellent yield, which encouraged us to develop a new synthesis of heterobimetallic arene complexes in order to investigate the influence of a cyclometallated manganese moiety on the migration of a $Cr(CO)_3$ fragment along a π-platform. A back migration was performed but yielded only to the starting material **31**.



Scheme 54: Synthesis of *N*-heterocyclic polyarene-$Cr(CO)_3$ complexes **30** and **31**

The introduction of this tetracarbonylmanganese fragment took place between the Fischer-carbene synthesis and the benzannulation reaction, affording the desired *N*-heterocyclic-polyarene heterobimetallic complex **34**. The haptotropic metal rearrangement was achieved by a thermal induction to produce the isomer **35** with chromium complexed to the terminal benzene ring of the polyarene as in the previous example (**Scheme 55**). The attempt of a light-induced back migration also failed and yielded to the starting material **35** in 30% yield.



Scheme 55 : Synthesis of cyclomanganated *N*-heterocyclic polyarene-$Cr(CO)_3$ complexes **34** and **35**

The intramolecular nature of the metal shift was established by NMR studies which revealed first order kinetics. The comparison of the NMR kinetic studies of the haptotropomerization in complex **30** and its simpler equivalent system **37**[88] indicates that the introduction of the *N*-heterocycle to the phenanthrene system slightly lowers the rate constant and slightly increases the free activation state. On the other hand, the *ortho*-manganation leads to an increase of the rate of the migration by a factor of 2 with a similar free activation enthalpy for the transition state (**Figure 30**). Nevertheless, the conversion yield is better without the $Mn(CO)_4$ fragment.

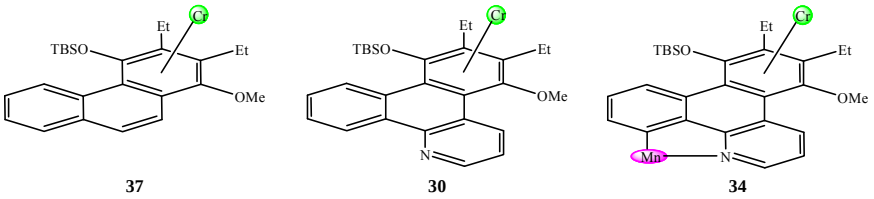


Figure 30: Comparison of NMR kinetic studies for **30**: rate constant k = (3.4 ± 0.1) x 10^{-3} s^{-1}, free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 103.6 ± 0.2 kJ.mol^{-1}, **34**: rate constant k = (10.7 ± 0.2) x 10^{-3} s^{-1}, free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 100.3 ± 0.2 kJ.mol^{-1} and **37**: rate constant k = (5.6 ± 0.6) x 10^{-3} s^{-1}, free activation enthalpy for the transition state $\Delta G^{\ddagger}$= 100.7 ± 0.3 kJ.mol^{-1}.

In summary, we developed several novel heterobimetallic complexes which in some cases undergo a thermally induced haptotropic migration of the chromium moiety along the π-face of the arene system. We obtained suitable crystals for X-ray analysis to characterize the organometallic structures.

4. Outlook

Formation of new heterobimetallic complexes bearing different metals (Rh, Ru, Pd…) allowing a possible haptotropic migration can be a major target of future studies. And in this regard, both systems can actually welcome new different moieties (**Figure 31**). A development of the coligand sphere of the different metal units by a ligand exchange could also play a great role in the control of the haptotropic migration as already shown in the case of (naphthalene)$Cr(CO)_3$. Further work on the reversibility of the haptotropic metal migration and the development of the protocole, which would make a molecular switch feasible, is of great interest.

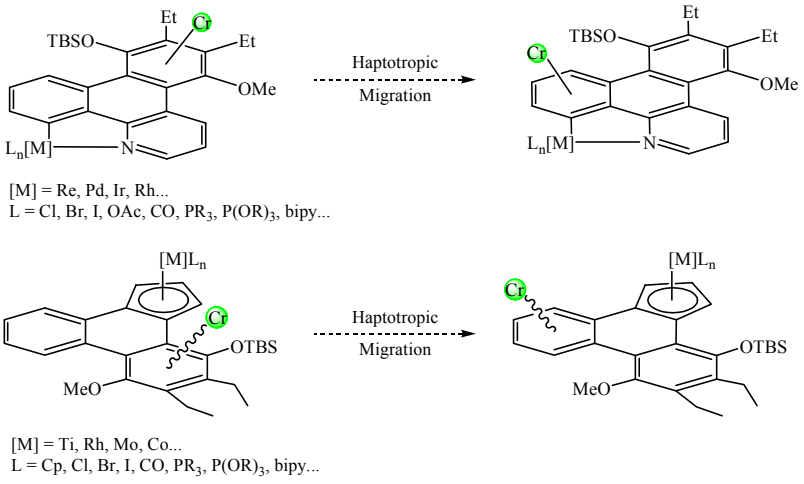


Figure 31: Novel heterobimetallic complexes allowing a possible haptotropic migration

V] CONCLUSION ET OUVERTURE

Une propriété caractéristique des complexes formés par des métaux de transition avec des ligands polycycliques aromatiques est leur capacité à se soumettre à des réarrangements haptotropiques ; le fragment métallique est considéré comme le groupe fonctionnel déplaçable qui migre entre deux cycles non équivalents du ligand hydrocarboné. Une deuxième unité métallique a été coordinée au squelette aromatique afin d'étudier son influence sur la migration du tricarbonylchrome. Dans ce contexte, les premiers complexes hétérobimétalliques tricarbonylchrome-tricarbonylmanganese et tricarbonylchrome-tricarbonylrhenium sur des polyarènes ont été synthétisés. De plus, la synthèse de nouveaux complexes cyclomanganatés du tricarbonylchrome sur un polyarène *N*-hétérocyclique a été etudiée. Dans tous ces travaux, la benzannulation [3+2+1] a été employé afin d'introduire l'entité du chrome sur le ligand.

1. Complexes hétérobimetalliques (benzo[*e*]indène)$Cr(CO)_3$-$Mn(CO)_3$

Les premiers complexes hétérobimetalliques ont été synthétisés de la façon suivante : La benzannulation de carbènes de Fischer portant une entité métallique supplémentaire produisait les produits hétérobimétalliques souhaités. Cette synthèse a débuté avec le 5-bromoindène (**Schéma 56**) et le 4-bromoindène (**Schéma 57**) afin de valider notre stratégie. Une nouvelle synthèse des complexes **3** et **4** du manganèse a été suivie par la formation des carbènes de Fischer **5** et **6** et de leur benzannulation; cette réaction a fourni les diastéréoisomères angulaires *anti*- **7** et **9** et *syn*- **8** et **10** des complexes hétérobimétalliques $Cr(CO)_3$-$Mn(CO)_3$. Une quelconque coopération entre les deux moitiés métalliques n'a pu être observée, que ce soit en analyses IR ou RMN, ou bien en cristallographie. D'une façon générale, il semble que l'inter conversion des groupes protecteurs (-Me et -TBS) n'affecte pas les structures cristallographiques des complexes (cependant il faudrait la structure du complexe **10** pour confirmer cette observation).

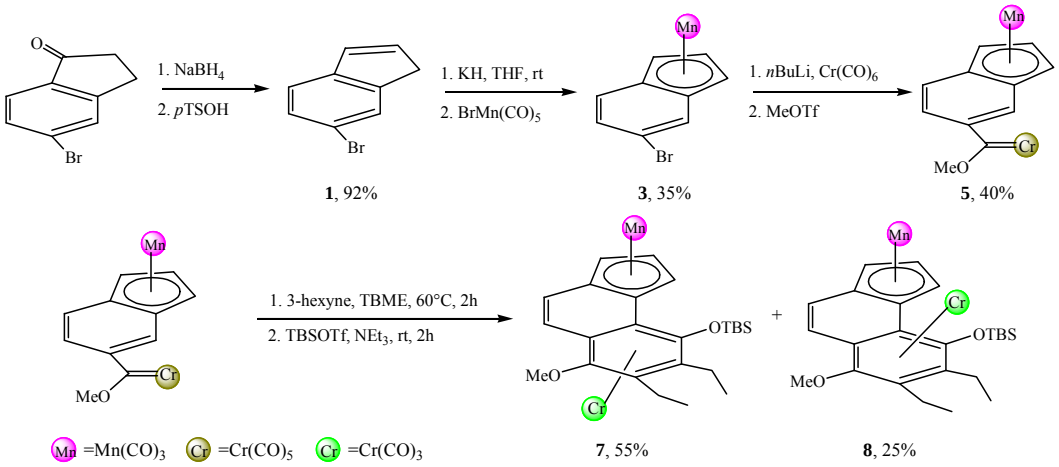


Schéma 56: Du 5-bromo-1-indanone aux complexes hétérobimetalliques (benzo[*e*]indène)$Cr(CO)_3$-$Mn(CO)_3$ **7** et **8**

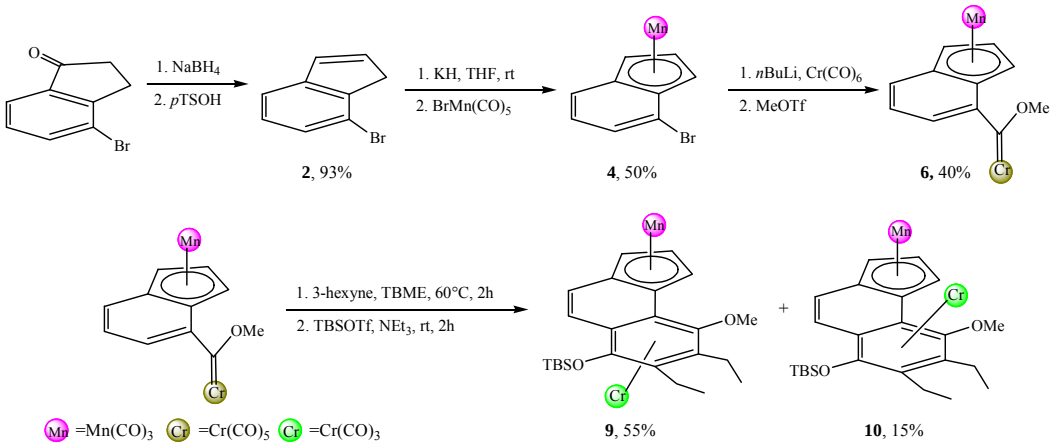
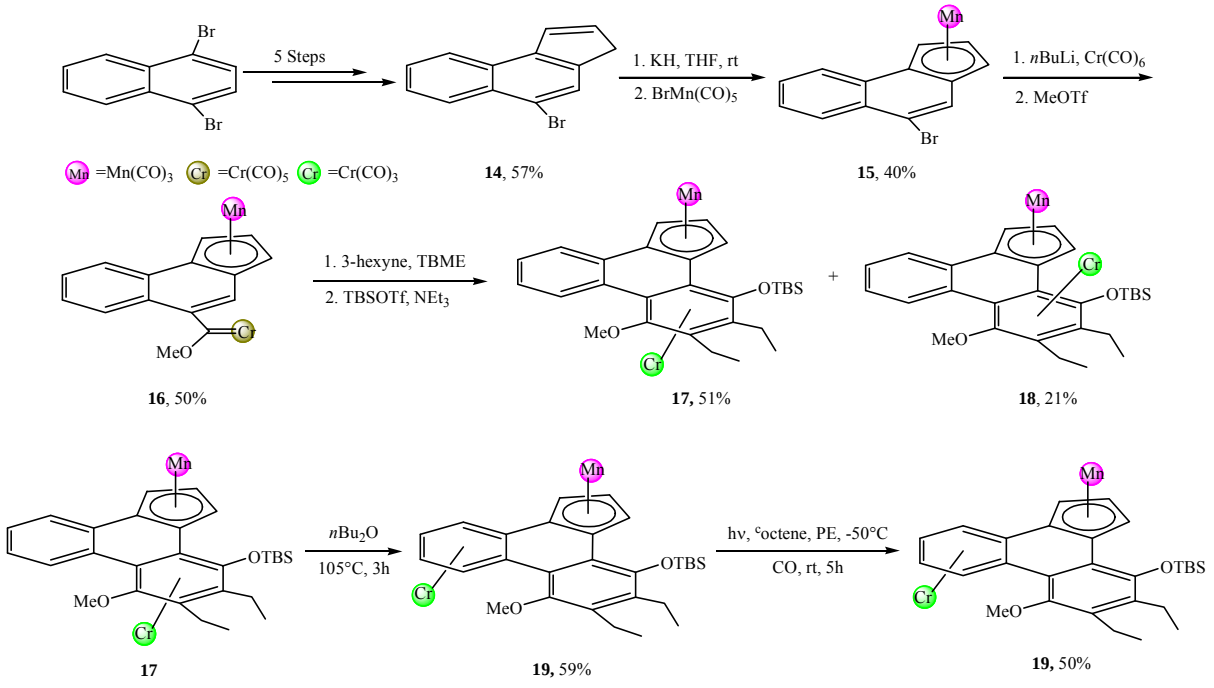


Schéma 57: Du 4-bromo-1-indanone aux complexes hétérobimetalliques (benzo[*e*]indène)$Cr(CO)_3$-$Mn(CO)_3$ **7** et **8**

2. Complexes hétérobimetalliques (dibenzo[*c*,*e*]indène)$Cr(CO)_3$-$Mn(CO)_3$ et (dibenzo[*c*,*e*]indène)$Cr(CO)_3$-$Re(CO)_3$

Les premiers essais concluants sur les complexes hétérobimétalliques (benzo[*e*]indene)$Cr(CO)_3$-$Mn(CO)_3$ nous ont conduits à développer une plateforme aromatique plus étendu qui permettrait une migration haptotropique. Tout d'abord, en partant du 1,4-dibromonaphthalene le ligand 8-bromobenzo[*e*]-1*H*-indène **14** a été synthétisé en 5 étapes pour un rendement de 57%. Ensuite, la même stratégie qu'employée précédemment a été suivi afin d'obtenir les complexes hétérobimétalliques **17** et **18**. Dans le système chrome-manganèse, la migration métallique haptotropique induite thermiquement a produit les haptotropomères **19** et **20** avec un rendement de 60% pour les deux isomères. La tentative de faire une permutation moléculaire réalisable via une migration retour induite par hν a conduit soit à l'isolation du produit de départ soit à sa décomposition (**Schéma 58**).



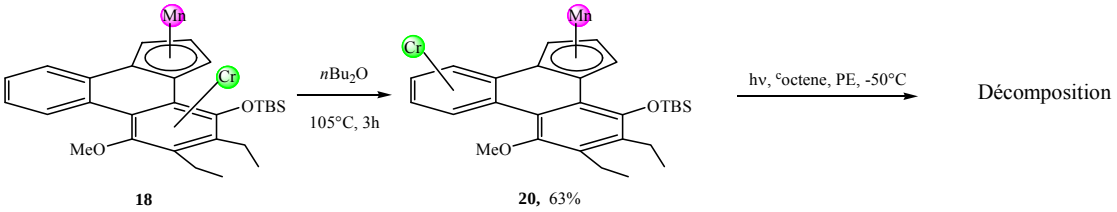


Schéma 58: Du 1,4-dibromonaphthalène aux complexes hétérobimetalliques (dibenzo[*c*,*e*]indène)$Cr(CO)_3$-$Mn(CO)_3$ **17**, **18**, **19** et **20**

Le déplacement intramoléculaire du chrome a été confirmé avec une étude cinétique par RMN de l'isomère *anti* **17** qui montre une réaction du premier ordre. L'interprétation des études cinétiques de l'haptotropomérisation du complexe *anti*-Cr-Mn **17** et du système équivalent plus simple **36**[88] montre clairement que l'introduction du cymanthrène sur le tricarbonyl(phénanthrène)chrome entraîne une augmentation considérable du $\Delta G^{\ddagger}$ et une diminution extrêmement importante de la vitesse de réaction (par un facteur 43) (**Figure 32**). Par conséquent, cette deuxième unité métallique défavorise mais cependant n'empêche pas le réarrangement métallotropique.

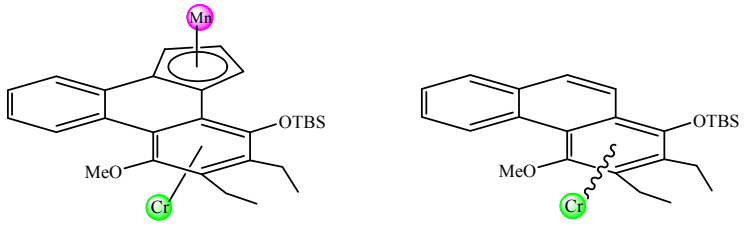


Figure 32: Comparaison des études cinétiques RMN pour **17**: constante de vitesse $k = (3.7 \pm 0.1) \times 10^{-5}$ s^{-1}, énergie d'activation pour l'état de transition $\Delta G^{\ddagger} = 120.3 \pm 0.2$ kJ.mol^{-1}et **36**: constante de vitesse $k = (1.6 \pm 0.2) \times 10^{-3}$ s^{-1}, énergie d'activation pour l'état de transition $\Delta G^{\ddagger} = 104.3 \pm 0.3$ kJ.mol^{-1}.

Nous avons ensuite décidé d'étendre notre système à un autre métal de transition, à savoir le rhénium qui se trouve dans la même colonne du tableau périodique que le manganèse et qui se complexe de la même façon aux ligands dérivés du cyclopentadiène. Nous avons utilisé avec succès la même procédure que précédemment pour synthétiser à notre connaissance les premiers complexes hétérobimetalliques du chrome et du rhénium (**Schéma 59**).

[88] K. H. Dötz, J. Stendel, Jr., S. Müller, M. Nieger, S. Ketrat, M. Dolg, *Organometallics*, **2005**, 24, 3219.

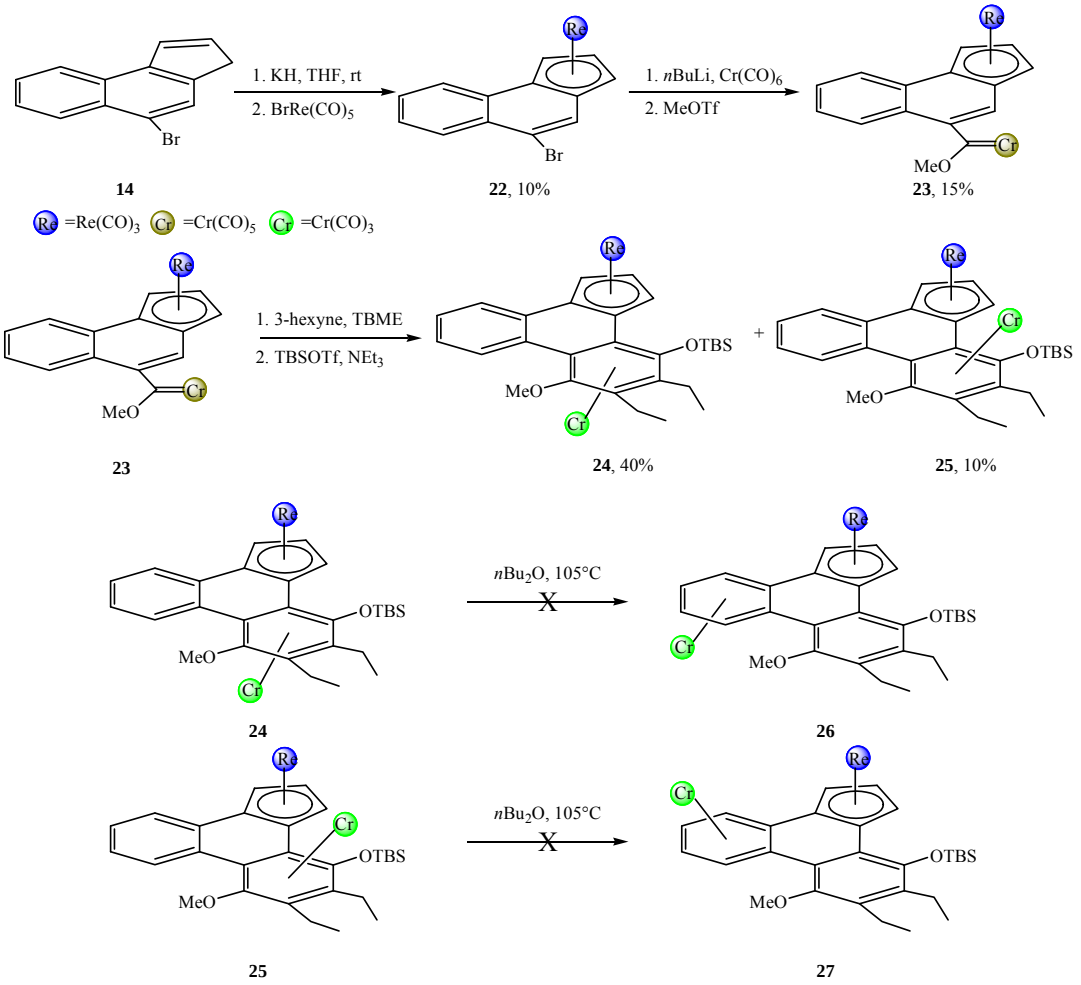


Schéma 59 : Du 1,4-dibromonaphthalène aux complexes hétérobimetalliques (dibenzo[*c*,*e*]indène)$Cr(CO)_3$-$Re(CO)_3$ **24** and **25**

3. Complexes (polyarène η^6-*N*-hétérocyclique)$Cr(CO)_3$ et complexes cyclomanganatés (polyarène η^6-*N*-hétérocyclique)$Cr(CO)_3$

Un carbène de Fischer a été synthétisé sur un polyarène *N*-hétérocyclique puis a été benzannulé avec succès (**Schéma 60**). Ensuite, une migration métallique haptotropique à été effectué pour produire l'haptotropomère **31** avec un excellent taux de conversion, ce qui nous a encouragé à développer une nouvelle voie de synthèse de complexes dinucléaires pour explorer l'influence d'un manganèse cyclométallaté sur la migration du chrome le long de la plateforme π-aromatique. Une migration retour a été tenté mais n'a mené qu'à l'isolation du produit de départ **31**.

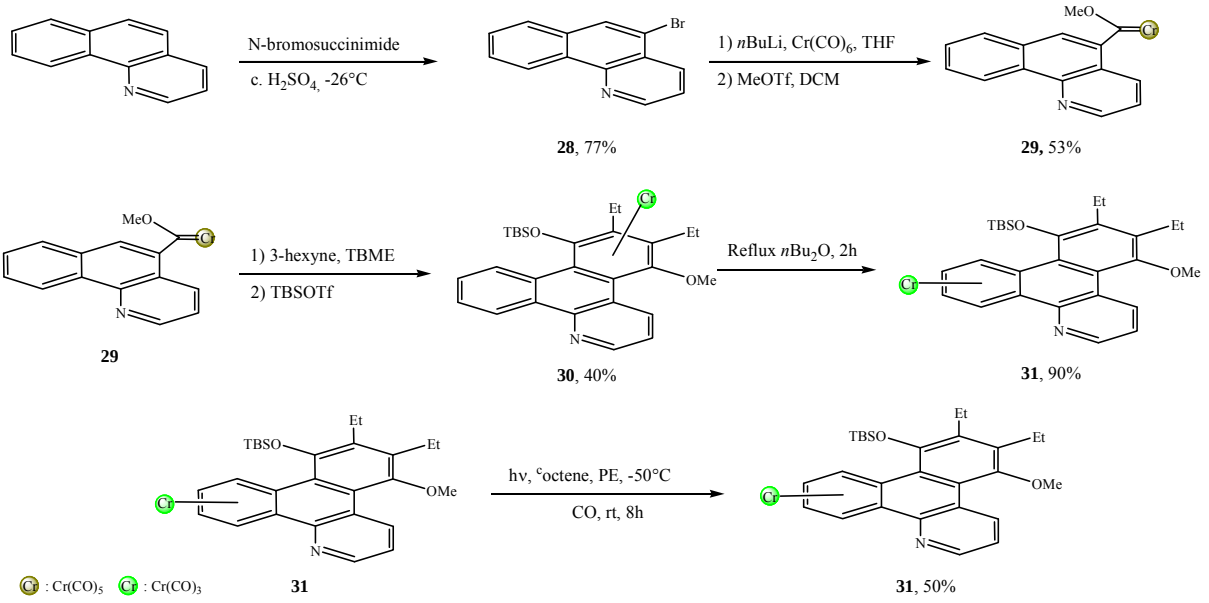


Schéma 60: Synthèse des complexes (polyarène *N*-hétérocyclique)$Cr(CO)_3$ **30** et **31**

L'introduction du tétracarbonylmanganèse a pris place entre la synthèse du carbène de Fischer et la réaction de benzannulation, produisant le complexe hétérobimetallique **34** sur un polyarène *N*-hétérocyclique. La migration haptotropique a été induite thermiquement pour fournir l'isomère **35** (**Schéma 61**). La tentative d'une migration retour a aussi échoué et mené à l'isolation du produit de départ.

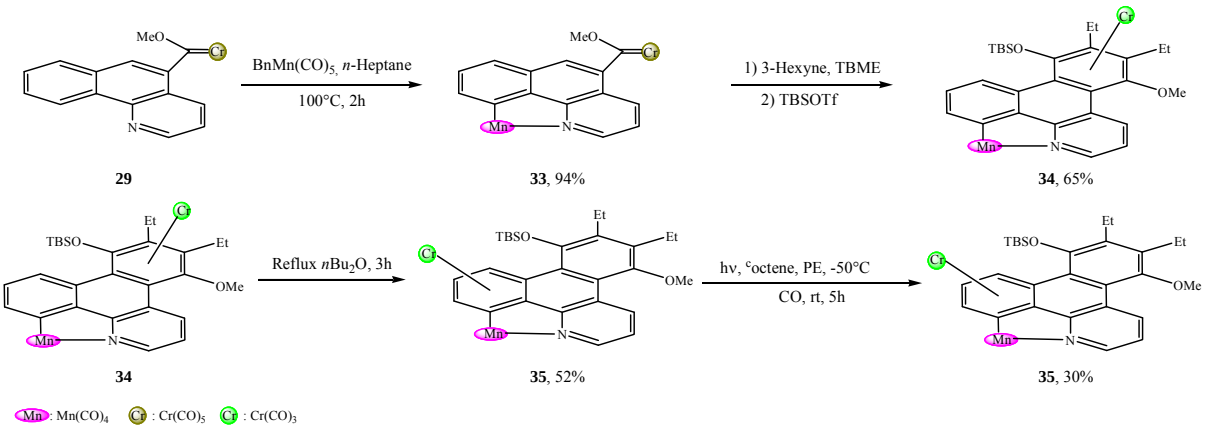


Schéma 61 : Synthèse des complexes cyclomanganatés (polyarène *N*-hétérocyclique)$Cr(CO)_3$ **34** et **35**

La nature intramoléculaire du déplacement métallique a été établi par une étude cinétique RMN qui révèle une réaction du premier ordre. L'interprétation de cette étude cinétique sur l'haptotropomérisation du complexe **30** et celle du complexe (phénanthrène)$Cr(CO)_3$ **37**[89] indiquent que l'introduction d'un hétéroarène sur le phénanthrène diminue légèrement la constante de vitesse de la réaction et augmente légèrement le $\Delta G^{\ddagger}$. En revanche, l'*ortho*-mangantion conduit à une augmentation de la constante de vitesse de la réaction de migration par un facteur 2 avec un $\Delta G^{\ddagger}$ similaire à celui rencontré dans le cas du phénanthrène (**Figure 33**). Néanmoins, la présence du manganèse réduit un peu le rendement du réarrangement.

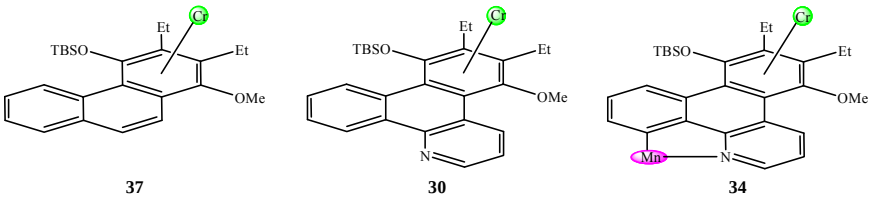


Figure 33: Comparison of NMR kinetic studies for **30**: constante de vitesse k = (3.4 ± 0.1) x 10^{-3} s^{-1}, énergie d'activation pour l'état de transition $\Delta G^{\ddagger}$= 103.6 ± 0.2 kJ.mol^{-1}, **34**: constante de vitesse k = (10.7 ± 0.2) x 10^{-3} s^{-1}, énergie d'activation pour l'état de transition $\Delta G^{\ddagger}$= 100.3 ± 0.2 kJ.mol^{-1} et **37**: constante de vitesse k = (5.6 ± 0.6) x 10^{-3} s^{-1}, énergie d'activation pour l'état de transition $\Delta G^{\ddagger}$= 100.7 ± 0.3 kJ.mol^{-1}.

En résumé, nous avons développé de nombreux nouveaux complexes hétérobimétalliques qui dans certains cas ont pu être soumis à une migration haptotropique du chrome thermiquement induite le long du système π-aromatique. Nous avons obtenus des cristaux de tous ces composés afin de déterminer précisément leurs structures organométalliques.

4. Ouverture

La formation de nouveaux complexes hétérobimétalliques portant différents métaux de transitions (Rh, Ru, Pd…) peut être intéressante pour aprofondir le sujet. Et dans ce sens, les deux systèmes étudiés dans ce travail peuvent accueillir de nouvelles entités métalliques (**Figure 34**). Un développement de la sphère de coligands des différents métaux par échange de ligand pourrait aussi jouer un grand rôle dans le contrôle de la migration haptotropique comme déjà démontré dans le cas du (naphthalène)$Cr(CO)_3$. Des études plus poussées sur la réversibilité du réarrangement et notamment le développement de son protocole, qui rendrait une permutation moléculaire réalisable, est de très grand intérêt.

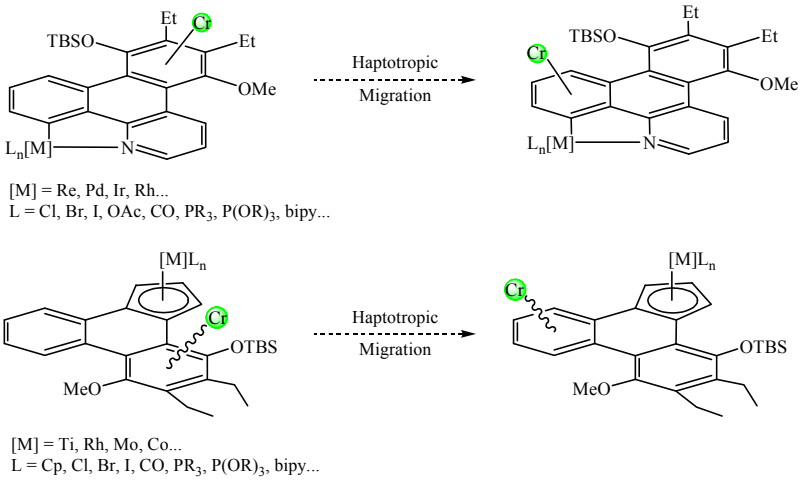


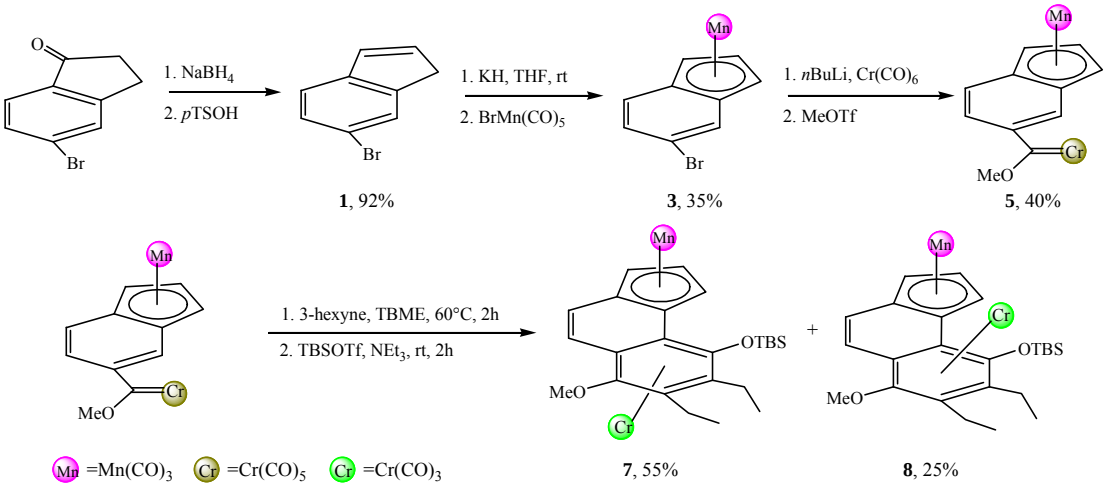
Figure 34: Nouveaux complexes hétérobimetalliques permettant une possible migration haptotropique

VII] ZUSAMMENFASSUNG UND AUSBLICK

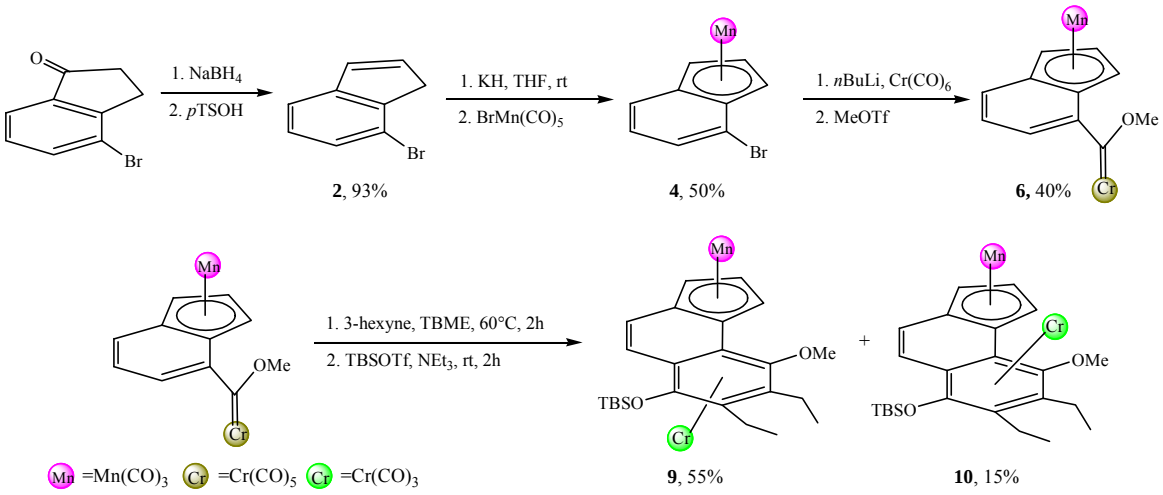
Typische Eigenschaft des Übergangsmetalls eines π-komplexes mit einer höhen Kondensierten Arengerüste ist deren Fähigkeit haptotrope Wanderung längs ausgedehnter π-Oberflächen durchzuführen. Das Metallfragment, das als bewegbare funktionelle Gruppe, ist über einen oder mehrere aromatische linge hinweg verschoben.
Wir untersuchen an heterobimetallischen Verbindungen, ob die Wanderung des Chromfragments auch durch ein primär eingebautes Metallzentrum gesteuert werden kann. Das heiβt, wir synthetisierten die erste heterobimetallischen Verbindungen $Cr(CO)_3$-$Mn(CO)_3$ und $Cr(CO)_3$-$Re(CO)_3$ aromatische Polyaren Komplexe.
Wir haben auβerdem auch eine neue Synthese von cyclischen-Mangan-(η^6-*N*-heterocyclische Polyaren)$Cr(CO)_3$ Komplexe erforscht. In allen Fällen ist die Chromtemplat-vermittelten Benzanellierung zum Einsatz gelangen, um das Chromfragment einzuführen.

1. Heterobimetallische benzo[*e*]inden $Cr(CO)_3$-$Mn(CO)_3$ Komplexen

Die erste bimetallische Komplexen wurden mit folgenden Strategie durchgeführt: Die Benzanellierung des Fischer-Carbens tragend zweites Metall führte zu den gewünschten heterobimetallischen Komplexe. Zuerst fing die Synthese des Komplexes mit 5-bromoinden (**Scheme 50**) und 4-bromoinden (**Scheme 51**) an, um unsere Strategie zu validieren. Eine neue Synthese des $Mn(CO)_3$-Komplexes **3** und **4** wurden durch die Chromtemplat-vermittelte-Benzanellierung der Fischer Carbene **5** und **6** gefolgt; Aus dieser Reaktion wurde angular *anti*- **7** und **9** und *syn*- **8** und **10** Diastereomere von heterobimetallische $Cr(CO)_3$-$Mn(CO)_3$ Komplexe bevorzugt. Weder in IR und NMR-Spektroskopien noch in Röntgenstrukturanalyse konnte eine Wechselwirkung zwischen die beiden Metalle beobachtet werden. Anscheint die Permutation zwischen den per-Substituenten (-Me und -TBDMS) beeinfluβt bzw. beeinträchtigt nicht die Kristallstruktur.



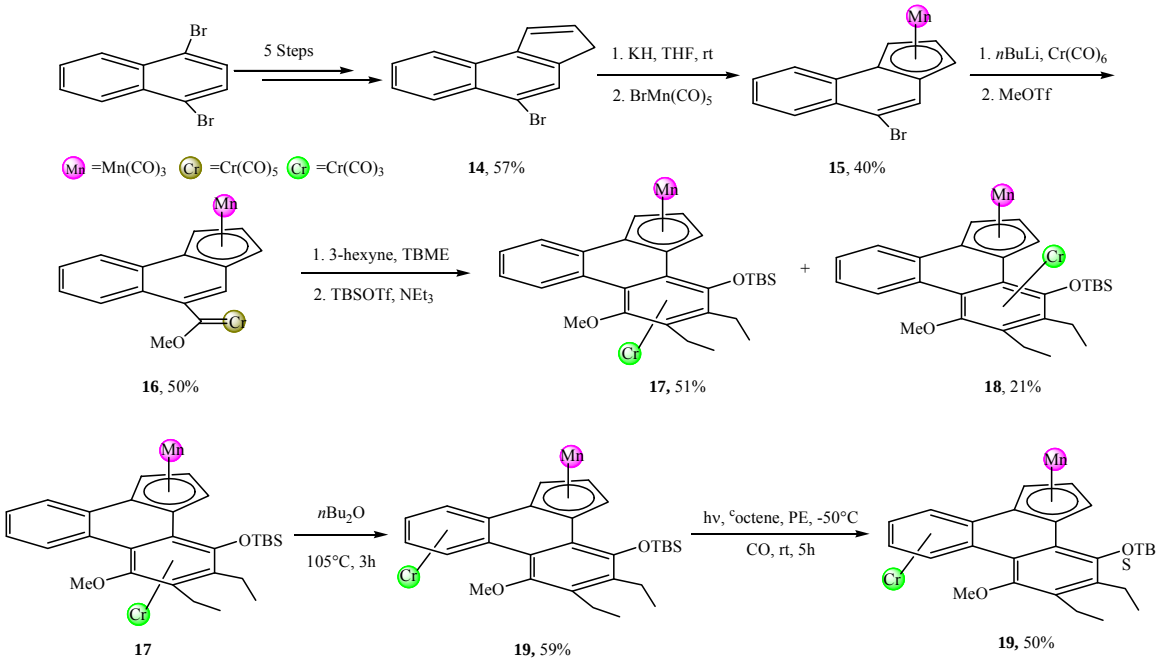
Scheme 62: Von 5-bromo-1-indanon zu heterobimetallische benzo[*e*]inden $Cr(CO)_3$-$Mn(CO)_3$ Komplexe **7** und **8**

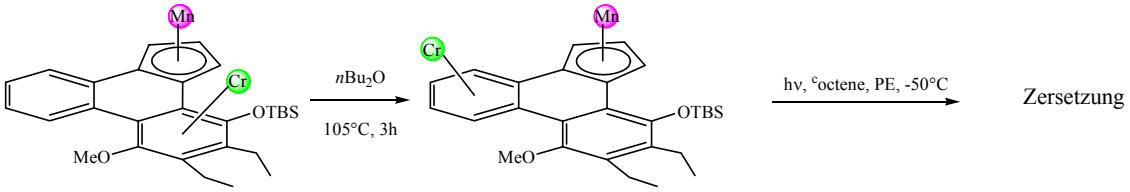


Scheme 63: Von 4-bromo-1-indanon to heterobimetallische benzo[*e*]inden $Cr(CO)_3$-$Mn(CO)_3$ Komplexe **9** and **10**

2. Heterobimetallische dibenzo[*c*,*e*]inden $Cr(CO)_3$-$Mn(CO)_3$ und $Cr(CO)_3$-$Re(CO)_3$ Komplexen

Diese erfolgreiche Resultat bei des Synthese des Heterobimetallische benzo[*e*]indene $Cr(CO)_3$-$Mn(CO)_3$ Komplexen hat uns ermütigt, die haptotrope Umlagerung an weiter ausgedehnten π-Oberfläschen zu untersuchen. Die Synthese fing auf diese Weise von 1,4-dibromonaphthalene mit über 5 Reaktions-Schritte, um 8-bromobenzo[*e*]-1*H*-inden **14** in 57% Ausbeute herzustellen. Für die Synthese der gewünschten Komplexen **17** und **18** wurden derselbe Reaktionsmechanismus verwendet. Die thermische induzierte haptotrope Wanderungen der Komplxen **19** und **20** wurden mit 60% Ausbeute erhalten. Der Versuch, eine Rückwanderung durch UV-Strahlung, war erfolglos und führte entweder zur Zersetzung oder zum Ausgangmaterial (**Scheme 52**).

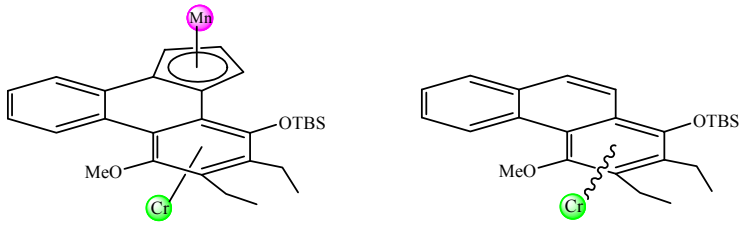




18 **20,** 63%

Scheme 64: Von 1,4-dibromonaphthalen zu heterobimetallische dibenzo[*c*,*e*]inden-$Cr(CO)_3$-$Mn(CO)_3$ Komplexe **17**, **18**, **19** und **20**

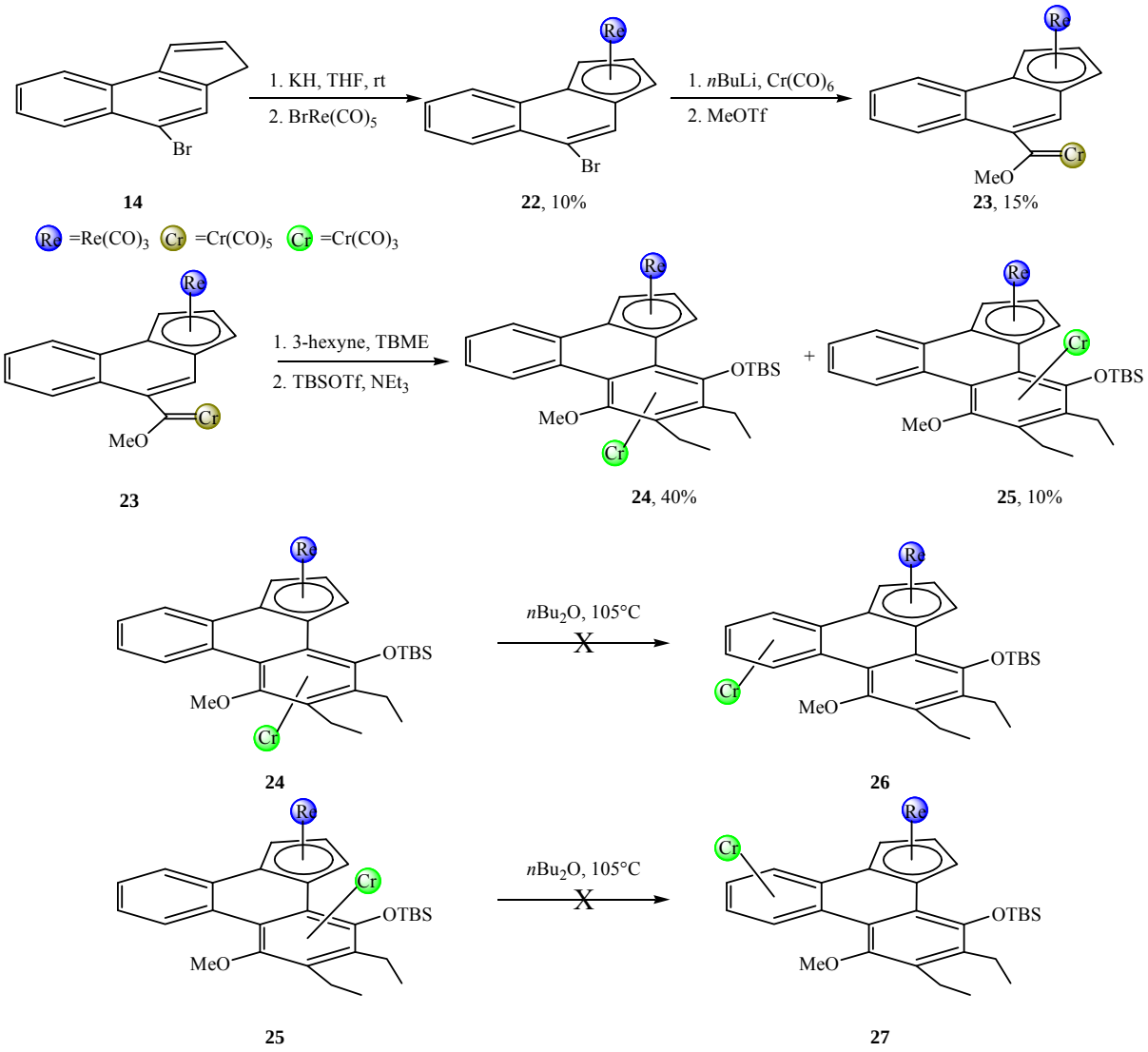
Die intramolekulare Umlagerung des Komplexes **17** zeigte durch NMR-Studie eine Reaktion erster Ordnung. Aus des Interpretation des NMR-Studien von Komplexe **17** und **36** wurden gezeigt, daβ die Einführung des Cymanthren-Fragments zu einer höheren $\Delta G^{\ddagger}$ fürhte und dabei die haptotrope Wanderung um Faktor 43 verlangsamte (**Figure 29**). In diesem Fall war das zweite Metall nicht bevorzugt, trotzdem wurde die haptotrope Umlagerung stattgefunden.



17 **36**

Abbildung 35: Vergleich des NMR-Studien für **17**: Geschwindigkeitskonstante k = (3.7 ± 0.1) x 10^{-5} s^{-1}, freie Aktivierungsenthalpie $\Delta G^{\ddagger}$= 120.3 ± 0.2 kJ.mol^{-1} und **36**: Geschwindigkeitskonstante k = (1.6 ± 0.2) x 10^{-3} s^{-1}, freie Aktivierungsenthalpie $\Delta G^{\ddagger}$= 104.3 ± 0.3 kJ.mol^{-1}.

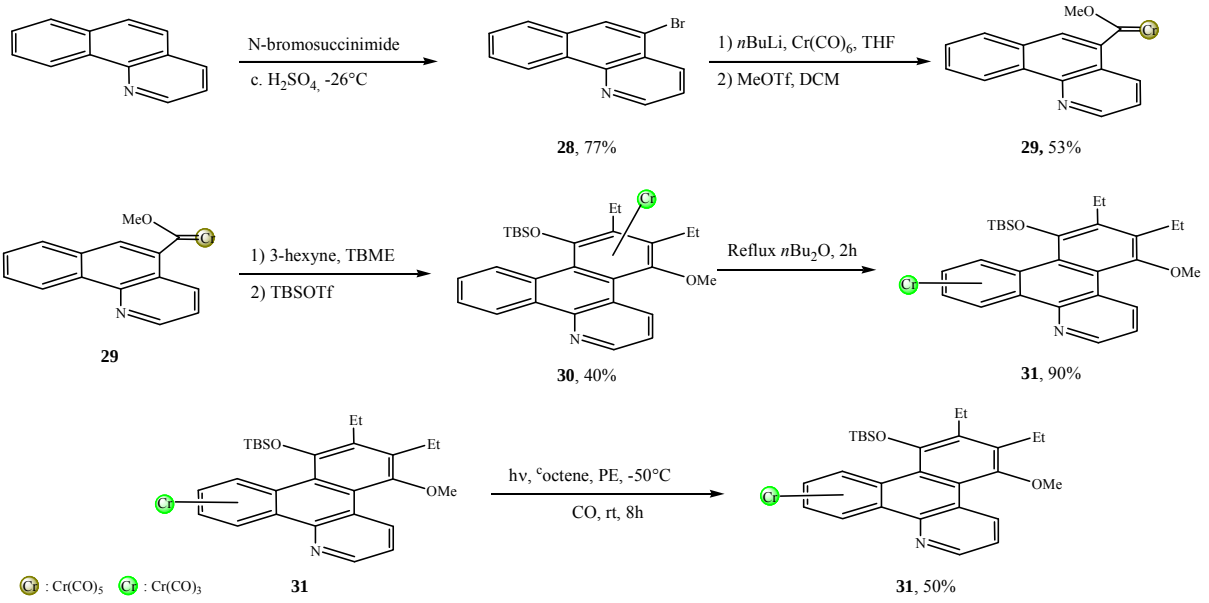
Ein weiteres Metall wie Rhenium wurde dann ins Auge gefasst, wegen derselbe Koordinationseigenschaft an Cp-Ligand zwischen Re und Mn. Dieselbe Procedure wurden für die Synthese von **24** und **25** angewendet. Leider wurden keine haptotrope Umlagerungen für Komplexe **24** und **25** beobachtet (**Scheme 53**).



Scheme 65 : Von 1,4-dibromonaphthalen zu heterobimetallische dibenzo[*c*,*e*]inden-$Cr(CO)_3$-$Re(CO)_3$ Komplexe **24** und **25**

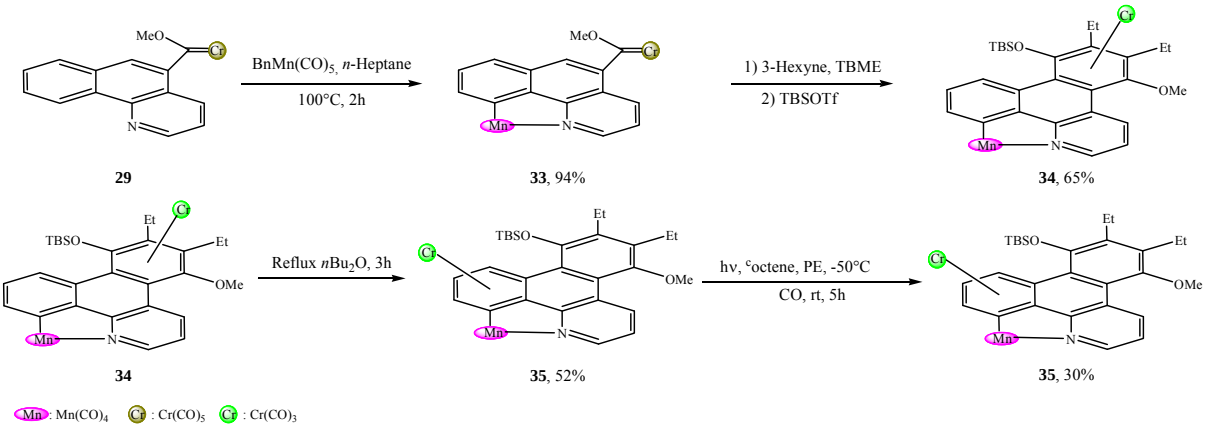
3. (η^6-*N*-heterocyclische-Polyaren)$Cr(CO)_3$ und cyclische-Mangan-(η^6-*N*-heterocyclische-Polyaren)$Cr(CO)_3$ Komplexe

Aus der *N*-heterocyclische Polyaren wurde Fischer-Carben synthetisiert, das weiter zur erfolgreichen Benzanellierung umgesetzt wurde. Die haptotrope Wanderung an *N*-heterocyclische Polyaren wurde auch durchgeführt und lieferte das Komplex **31** in gute Ausbeute, wobei eine neue Synthese von heterobimetallischen Komplexen an diesem System ins Auge gefasst wurde, um der Einfluß des Manganfragments auf die haptotrope Umlagerung des Chromtricarbonylfragments entlang des π-Systems zu untersuchen. Die Rückwanderung führte leider zum Ausgangmaterial **31** zurück (**Scheme 54**).



Scheme 66: Synthese von (*N*-heterocyclische Polyaren)$Cr(CO)_3$ Komplexe **30** und **31**

Die Insertion des Tetracarbonylmangan-Fragments war zwischen der Fischer-Carben-Stufe und die Benzanellierung stattfinden, was zu der Bildung des gewünschten heterobimetallische *N*-heterocyclische Polyaren Komplexes **34** führte. Durch die thermische Induktion wurde die haptotrope Wanderung in Richtung des terminalen Ringes der Polyaren realisiert (**Scheme 67**). Der Versuch durch UV-Strahlung, um die Rückwanderung durchzuführen, war erfolglos und das Ausgangsmaterial liest sich wieder in 30% Ausbeute rückgewinnen.



Scheme 67 : Synthese von cyclischen-Mangan-(*N*-heterocyclische-Polyaren)$Cr(CO)_3$ Komplexe **34** und **35**

Diese intramolekulare Metallverschiebung wurde durch NMR-Studie etabliert und gehorchte eine Reaktion erster Ordnung. Der NMR-Vergleich der Haptotropomere **30** und **37** zeigten gewisse Erniedrigung der Geschwindigkeitskonstante und Erhöhung der freie Aktivierungsenthalpie. Auf der andere Seite, durch die Einführung des Mangans an der *ortho*-Position führt zu einer Erhöhung der Umlagerungsgeschwindigkeit um Faktor 2 (**Figure 30**). Trotzdem ist die Umsetzungsausbeute besser ohne die Anwesenheit des $Mn(CO)_4$-Fragments.

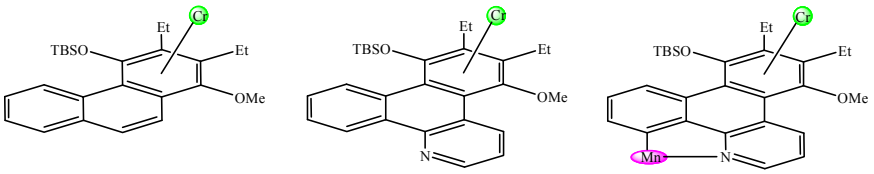


Abbildung 36: Vergleich des NMR-Studien für **30**: Geschwindigkeitskonstante k = (3.4 ± 0.1) x 10^{-3} s^{-1}, freie Aktivierungsenthalpie $\Delta G^{\ddagger}$= 103.6 ± 0.2 kJ.mol^{-1}, **34**: Geschwindigkeitskonstante k = (10.7 ± 0.2) x 10^{-3} s^{-1}, freie Aktivierungsenthalpie $\Delta G^{\ddagger}$= 100.3 ± 0.2 kJ.mol^{-1} und **37**: Geschwindigkeitskonstante k = (5.6 ± 0.6) x 10^{-3} s^{-1}, freie Aktivierungsenthalpie $\Delta G^{\ddagger}$= 100.7 ± 0.3 kJ.mol^{-1}.

In der Zusammenfassung haben wir neue verschiedene heterobimetallische Komplexe entwickelt, die durch die thermische Induktion eine haptotrope Wanderung entlang der π-Oberfläche durchführten. Die metallorganischen Strukturen konnten durch Röntgenstrukturanalyse bestimmt und charakterisiert werden.

4. Ausblick

Die Darstellung von neuen heterobimetallische Komplexen mit Rhenium, Ruthenium oder Palladium als Zentralmetall eröffnet dabei eine neue Studie zur haptotrope Wanderung. Die Modifikation der Coligandsphäre durch Ligandaustausch spielt auch eine groβe Rolle in der haptotrope Wanderung. Eine reversible Induktion der Metallwanderung, die den Weg zum molekulare Schalter eröffnet, ist von besonderem Interesse.

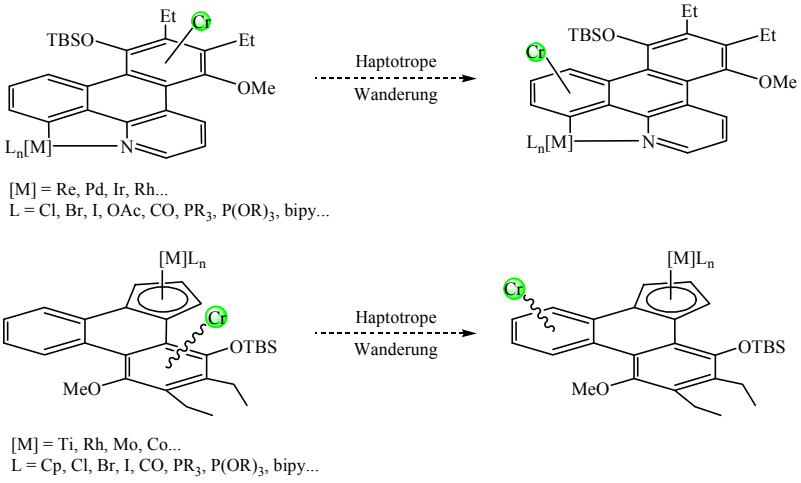


Abbildung 37: Haptotrope Wanderung neuer heterobimetallischen Komplexe

VII] EXPERIMENTAL PART

1. General Considerations and abbreviations

All experiments involving organometallic compounds were carried out under argon atmosphere by using standard schlenk techniques.

All temperatures mentioned are temperatures measured from oil, water or cooling bath.

Solvents were distilled, dried using standard methods, saturated and stored under argon.

Chromatographic columns were performed with degassed *Macherey Nagel* silica gel MN 60 (0.015-0.025 mm).

^{1}H and ^{13}C NMR spectra were recorded on *Brucker DRX 500* at room temperature. Deuterated solvents were all stored in fridge and used as received for organic compounds and pump-freeze-thaw three times for organometallic compounds. Abbreviations for intensities of ^{1}H-NMR signals:
s = singulet, d = doublet, t = triplet, m = multiplet, pt = pseudo-triplet, s_{br} = broad signal.

IR spectra were majored with a *Nicolet Magna 550 FT* spectrometer in petroleum ether. Abbreviations for intensities of IR bands:
w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

Mass spectra (FAB+ and EI) were recorded on a *MS 50* from *Kratos*.

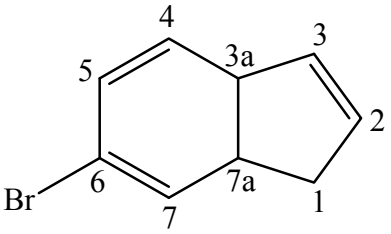
Melting points were determined with a *Reichert Austria* apparatus.

Other abbreviations:

δ = chemical shift, NMR = nuclear magnetic resonance, ^{1}H = proton NMR, ^{13}C = carbon NMR, °C = Celsius degree, cm^{-1} = wave number, DCM = dichloromethane, DMSO = dimethylsulfoxide, Et_2O = diethyl ether, PE = petroleum ether, TBME = *tert*-butyl-methyl ether, THF = tetrahydrofuran, EI = electronic ionisation, FAB = fast atom bombardement, g = gramm, h = hour, Hz = frequency, *J* = coupling constant, L = ligand, M = molecular mass, M^{+} = molecular ion, m/z = mass to charge ratio, mL = milliliter, min = minute, MS = mass spectroscopy, R_f = retention factor, rt = room temperature.

2. Spectroscopic analyses

6-bromo-1*H*-indene (1)



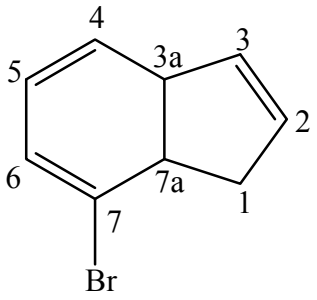
C_9H_9Br
Mol. Wt.: 197,07 g/mol

Yield: 92%.
R_f: 0.52 (PE).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 3.22 (2H, s_{br}, CH_2), 6.38 (1H, dt, ^3J= 6.5 Hz, ^3J= 1.9 Hz, H2), 6.68 (1H, dt, ^3J= 6.5 Hz, H3), 7.10 (1H, d, ^3J= 8.0 Hz, H4), 7.25 (1H, dd, ^3J= 8.0 Hz, ^4J= 1.1 Hz, H5), 7.44 (1H, d, ^4J= 1.1 Hz, H7).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 39.1 (C1), 118.7 (C6), 122.2 (C4), 127.1 (C5), 129.3 (C7), 131.5 (C3), 134.7 (C2), 143.8 (C3a), 145.8 (C7a).

7-bromo-1*H*-indene (2)



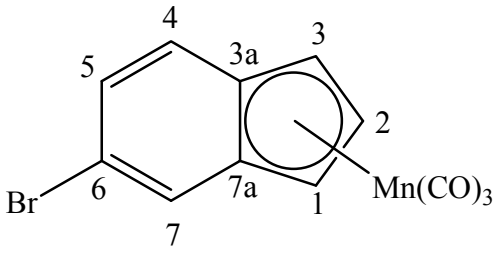
C_9H_9Br
Mol. Wt.: 197,07 g/mol

Yield: 93%.
R_f: 0.70 (PE).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 3.23 (2H, s, CH_2), 6.42 (1H, dt, ^3J= 7.6 Hz, ^3J= 1.9 Hz, H2), 6.74 (1H, dt, ^3J= 5.5 Hz, H3), 7.01 (1H, dd, ^3J= 8.0 Hz, H5), 7.24 (2H, m, H4 and H6).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 49.1 (C1), 119.0 (C7), 120.1 (C4), 127.9 (C5), 128.3 (C6), 132.1 (C3), 134.8 (C2), 143.9 (C7a), 146.4 (C3a).

Tricarbonyl-[ŋ^5-1,2,3,3a,7a-(6-bromoindenyl)]manganese (3)



$C_{12}H_6BrMnO_3$
Mol. Wt.: 333,02 g/mol

KH (0.70 g, 17.5 mmol) is added to a solution of the 6-bromo-1*H*-indene ligand **1** (3.4 g, 17.4 mmol) in 15 mL of freshly distilled absolute THF and stirred for one hour at room temperature under argon. Then $BrMn(CO)_5$ (4.95 g, 18.0 mmol) is charged in the shlenk tube and the reaction is stirred overnight at room temperature. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3:1) affords 2.0 g of complex **3** (35%) as an air-sensitive yellow product.

Yield: 35%.
R_f: 0.60 (PE/DCM 3:1).
m.p.: 60°C.

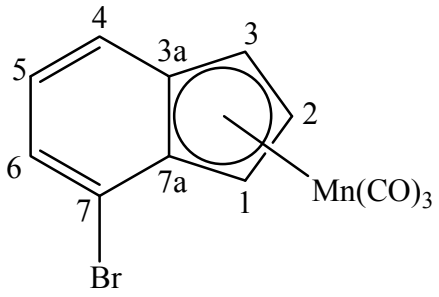
IR (petroleum ether): ν(CO) 2026 (s), 1949 (vs) cm^{-1}.

^{1}H-NMR (500 MHz, aceton): δ (ppm) 5.27 (1H, dd, ^3J= 2.8Hz, ^3J= 2.75Hz, H2), 5.52 (2H, m, H1 and H3), 7.25 (1H, dd, ^4J= 1.5Hz, ^3J= 9.1Hz, H5), 7.61 (1H, d, ^3J= 9.1Hz, H4), 7.85 (1H, s_{br}, H7).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) 71.7, 72.3, 89.3 (C1-C3), 101.7, 105.6, 120.4 (C3a, C6, C7a), 126.8, 127.5, 130.5 (C4, C5 and C7), 224.9 ($Mn(CO)_3$).

MS (FAB): *m/z* 331.9 [M^+, 54], 303.9 [M^+ -1CO, 41], 277.9 [M^+ -2CO, 99], 247.9 [M^+ -3CO, 64].

Tricarbonyl-[η^5-1,2,3,3a,7a-(7-bromoindenyl)]manganese (4)



$C_{12}H_6BrMnO_3$
Mol. Wt.: 333,0163

KH (0.90 g, 22.5 mmol) is added to a solution of the 7-bromo-1*H*-indene ligand **2** (4.3 g, 22.05 mmol) in 25 mL of freshly distilled absolute THF and stirred for one hour at room temperature under argon. Then $BrMn(CO)_5$ (6.18 g, 22.5 mmol) is charged in the shlenk tube and the reaction is stirred overnight at room temperature. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3/1) affords 3.64 g of complex **4** (50%) as an air-sensitive yellow product.

Yield: 50%.
R_f: 0.60 (PE/DCM 3:1).
m.p.: 75°C.

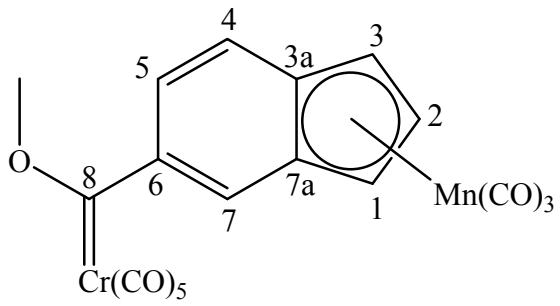
IR (petroleum ether): ν(CO) 2028 (s), 1946 (vs) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 5.12 (1H, s_{br}, H2), 5.35-5.37 (2H, m, H1 and H3), 7.04 (1H, m, ArH), 7.37 (1H, d, ^3J= 7.1 Hz, ArH), 7.51 (1H, d, ^3J= 8.4 Hz, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) 72.7, 72.9 (C1, C3), 89.0 (C2), 104.4, 105.6 (C3a, C7a), 119.9 (C7), 124.4, 127.4, 128.7 (C4-C6), 224.6 ($Mn(CO)_3$).

MS (EI): *m/z* 331.8 [M^+, 13], 303.8 [M^+ -1CO, 6], 275.9 [M^+ -2CO, 21], 247.9 [M^+ -3CO, 99], 192.9 [M^+ -Mn -3CO, 3].

Tricarbonyl-{pentacarbonyl[6-indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,7a]}manganese (5)



$C_{19}H_9CrMnO_9$
Mol. Wt.: 488,20 g/mol

The tricarbonyl-[ŋ^5-1,2,3,3a,7a-(6-bromoindenyl)]manganese complex **3** (2.0 g, 6.0 mmol) is dissolved in 50 mL of freshly distilled absolute THF to give a yellow solution. At -78°C is added drop by drop *n*-BuLi, a 2.5 M solution in hexane (2.4 mL, 6.0 mmol), the solution becomes immediately brown, and five minutes later $Cr(CO)_6$ (1.37 g, 6.2 mmol) is added. The solution is allowed to reach 20°C within an hour and then the solvent is evaporated via a vacuum pump. The resulting brown oil is then dissolved in 50 mL of absolute dichloromethane and cooled down to -50°C. Methyltriflate (1.97 g, 12.0 mmol) is added drop by drop to the solution which is then warmed to room temperature within half an hour and stirred an extra hour. The solution becomes deep dark red. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3:1) affords 2.0 g of complex **5** as an air-sensitive dark red product.

Yield: 40%.
R_f: 0.55 (PE/DCM 3:1).
m.p.: decomposition.

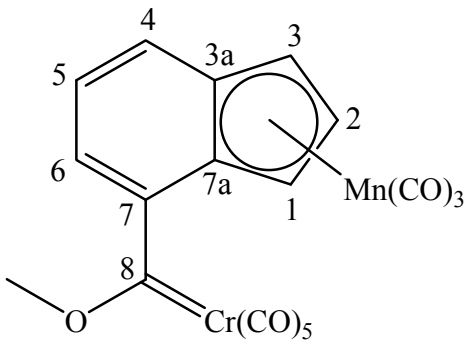
IR (petroleum ether): ν(CO) 2063 (m), 2027 (s), 1955 (s), 1947 (s) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 4.65 (s, 3H, OCH_3), 5.15 (1H, d, CpH), 5.26-5.37 (2H, m, CpH), 7.05 (1H, d, ^3J= 8.9Hz, ArH), 7.41 (1H, s_{br}, ArH), 7.51 (1H, d, ^3J= 8.9Hz, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) 67.4 (OCH_3), 71.4, 73.8, 90.0 (C1-C3), 101.1, 104.5 (C3a, C7a), 121.0 (C6), 122.0, 125.1 (C4, C5, C7), 216.0 (4 *trans*-Cr(CO)), 224.2 (1 *cis*-Cr(CO)), 224.4 ($Mn(CO)_3$), 348.5 (C8).

MS (FAB): *m/z* 487.9 [M^+, 19], 431.9 [M^+ -2CO, 54], 403.9 [M^+ -3CO, 30], 375.9 [M^+ -4CO, 99], 347.9 [M^+ -5CO, 75], 263.9 [M^+ -8CO, 8].

Tricarbonyl-{pentacarbonyl[7-indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,7a]}manganese (6)



$C_{19}H_9CrMnO_9$
Mol. Wt.: 488,20 g/mol

The tricarbonyl-[ŋ^5-1,2,3,3a,7a-(7-bromoindenyl)]manganese complex **4** (1.60 g, 4.8 mmol) is dissolved in 40 mL of freshly distilled absolute THF to give a yellow solution. At -78°C is added drop by drop *n*-BuLi, a 2.5 M solution in hexane (1.92 mL, 4.8 mmol), the solution becomes immediately brown, and five minutes later $Cr(CO)_6$ (1.1 g, 5.0 mmol) is added. The solution is allowed to reach 20°C within an hour and then the solvent is evaporated via a vacuum pump. The resulting brown oil is then dissolved in 40 mL of absolute dichloromethane and cooled down to -50°C. Methyltriflate (1.09 g, 9.6 mmol) is added drop by drop to the solution which is then warmed to room temperature within half an hour and stirred an extra hour. The solution becomes deep dark red. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3:1) affords 0.94 g of complex **6** as an air-sensitive dark red product.

Yield: 40%.
R_f: 0.50 (PE/DCM 3:1).
m.p.: decomposition.

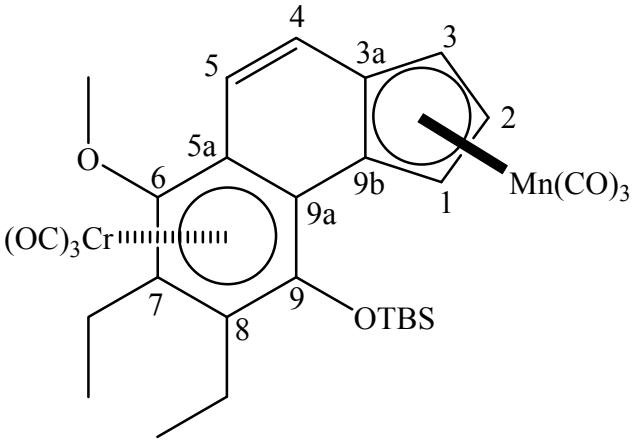
IR (petroleum ether): ν(CO) 2064 (A1, m), 2027 (s), 1954 (E, s), 1945 (s) cm^{-1}.

^{1}H-NMR (500 MHz, aceton-d6): δ (ppm) 5.16 (s, 3H, OCH_3), 5.30 (1H, m, CpH), 5.54 (1H, s_{br}, CpH), 5.57 (1H, s_{br}, CpH), 7.44 (1H, dd, ^{3}J= 8.1Hz, ^3J= 7.6Hz, ArH), 7.78-7.81 (2H, m, ArH).

^{13}C-NMR (100 MHz, aceton-d6): δ (ppm) 68.9 (OCH_3), 73.3, 75.2, 90.4 (C1-C3), 97.3, 105.3 (C3a, C7a), 126.9, 130.3 (C4, C5, C6), 131.3 (C7), 217.1 (4 *trans*-Cr(CO)), 225.2 (1 *cis*-Cr(CO)), 225.7 ($Mn(CO)_3$), 347.4 (C8).

MS (EI): *m/z* 487.9 [M^+, 10], 459.9 [M^+ -CO, 3], 431.9 [M^+ -2CO, 12], 403.9 [M^+ -3CO, 27], 375.9 [M^+ -4CO, 23], 347.9 [M^+ -5CO, 89], 320.0 [M^+ -6CO, 13], 292.0 [M^+ -7CO, 97], 264.0 [M^+ -8CO, 100].

***Anti*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-6-methoxy-9-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese (7)**



$C_{30}H_{33}CrMnO_8Si$
Mol. Wt.: 656,60 g/mol

A solution of the tricarbonyl-{pentacarbonyl[6-indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,7a]}manganese complex **5** (0.087 g, 0.178 mmol) and 3-hexyne (0.058 g, 0.173 mmol) in 5 mL *tert*-butyl-methylether is warmed to 65°C (oil bath temperature) for two hours. Then the phenolic group is protected at room temperature by addition of triethylamine (0.046 g, 0.713 mmol) and *tert*-butyl-dimethylsilyl triflate (0.188 g, 0.713 mmol). After stirring for two hours, chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (1:1) affords first 0.0485 g of anti complex **7** (55%) followed by 0.0256 g of syn complex **8** (30%) as air-sensitive orange products. Recrystallisation from dichloromethane at 4°C produces crystals suitable for X-ray analysis.

Yield: 55%.
R_f: 0.26 (PE/DCM 1:1).
m.p.: 160°C.

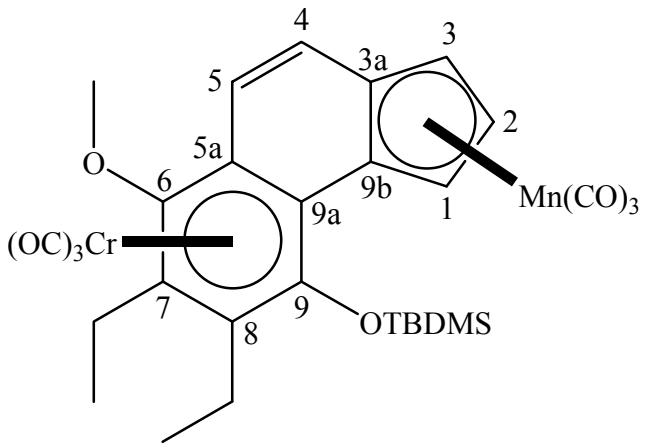
IR (petroleum ether): ν(CO) 2025 (vs), 1963 (s), 1948 (vs), 1903 (m), 1890 (m) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.48 (3H, s, $SiCH_3$), 0.65 (3H, s, $SiCH_3$), 1.17 (9H, s, $SiC(CH_3)_3$), 1.25 (3H, t, ^3J=7.4 Hz, CH_2CH_3), 1.34 (3H, t, ^3J=7.5 Hz, CH_2CH_3), 2.53-2.59 (3H, m, CH_2CH_3, CH_2CH_3), 2.98 (1H, dt, ^2J=15.0 Hz, ^3J= 7.5 Hz, CH_2CH_3), 3.78 (3H, s, OCH_3), 4.96 (1H, pt, ^3J=2.9 Hz, CpH), 5.26 (1H, m, CpH), 6.04 (1H, m, CpH), 7.14 (1H, m, H4 or H5), 7.38 (1H, d, ^3J= 9.4 Hz, H4 or H5).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -1.4 ($SiCH_3$), 0.3 ($SiCH_3$), 15.8 (CH_2CH_3), 17.4 (CH_2CH_3), 19.4 ($SiC(CH_3)_3$), 20.5 (CH_2CH_3), 20.9 (CH_2CH_3), 26.3 ($SiC(CH_3)_3$), 63.6 (OCH_3), 76.8 (C2), 80.9, 84.4 (C1, C3), 92.1, 102.3, 103.5, 106.2, 110.9 (5 ArC),122.3, 124.6 (C4, C5), 137.0 (ArC), 224.9 ($Mn(CO_3)$), 234.0 ($Cr(CO_3)$).

MS (EI): *m/z* 656.0 [M^+, 15], 598.9 [M^+ -2CO, 4], 572.0 [M^+ -3CO, 39], 520.1 [M^+ -3CO -Cr, 10], 488.0 [M^+ -6CO, 41], 436.1 [M^+ -6CO -Cr, 100], 382.2 [M^+ -6CO -Cr -Mn, 14].

***Syn*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-6-methoxy-9-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese (8)**



$C_{30}H_{33}CrMnO_8Si$
Mol. Wt.: 656,60 g/mol

Yield: 30%.
R_f: 0.15 (PE/DCM 1:1).
m.p.: 134°C.

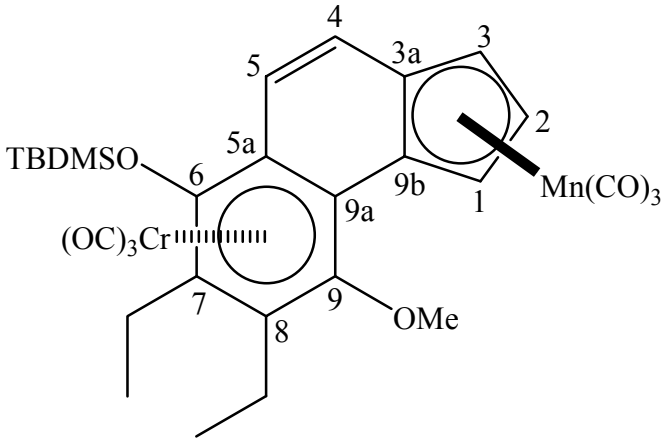
IR (petroleum ether): ν(CO) 2031 (vs), 1965 (s), 1946 (m), 1890 (w), 1886 (m) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) -0.24 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.01 (9H, s, $SiC(CH_3)_3$), 1.20 (3H, t, ^3J=7.1 Hz, CH_2CH_3), 1.37 (3H, t, ^3J=7.0 Hz, CH_2CH_3), 2.25-2.88 (4H, m, CH_2CH_3, CH_2CH_3), 3.86 (3H, s, OCH_3), 4.87-4.94 (2H, m, CpH), 6.14 (1H, s_{br}, CpH), 7.36-7.44 (2H, m, H4 and H5).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -1.2 ($SiCH_3$), -0.1 ($SiCH_3$), 14.6 (CH_2CH_3), 19.2 (CH_2CH_3), 19.5 ($SiC(CH_3)_3$), 20.2 (CH_2CH_3), 21.8 (CH_2CH_3), 26.3 ($SiC(CH_3)_3$), 67.4 (OCH_3), 72.6 (C2), 81.4, 83.2 (C1, C3), 87.5, 100.9, 101.3, 103.1, 103.8, 113.2 (6 ArC), 122.6 (C4 or C5), 127.8 (ArC), 128.0 (C4 or C5), 140.7 (ArC), 224.5 ($Mn(CO_3)$), 234.0 ($Cr(CO_3)$).

MS (EI): *m/z* 656.0 [M^+, 19], 572.0 [M^+ -3CO, 7], 520.0 [M^+ -3CO -Cr, 9], 488.0 [M^+ -6CO, 6], 436.1 [M^+ -6CO -Cr, 100], 382.2 [M^+ -6CO -Cr -Mn, 2].

***Anti*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-9-methoxy-6-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese (9)**



$C_{30}H_{33}CrMnO_8Si$
Mol. Wt.: 656,60 g/mol

A solution of tricarbonyl-{pentacarbonyl[7-indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,7a]}manganese complex **6** (0.40 g, 0.82 mmol) and 3-hexyne (0.27 g, 3.28 mmol) in 20 mL *tert*-butyl-methylether is warmed to 65°C (oil bath temperature) for two hours. Then the phenolic group is protected at room temperature by addition of triethylamine (0.21 g, 3.28 mmol) and *tert*-butyl-dimethylsilyl triflate (0.86 g, 3.28 mmol). After stirring for two hours, chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3/1) affords first 0.30 g of anti complex **9** (55.5%) followed by 0.08 g of syn complex **10** (14.5%) as air-sensitive orange products. Recrystallisation from dichloromethane at 4°C produces crystals suitable for X-ray analysis.

Yield: 55.5%.
R_f: 0.40 (PE/DCM 3:1).
m.p.: 178°C.

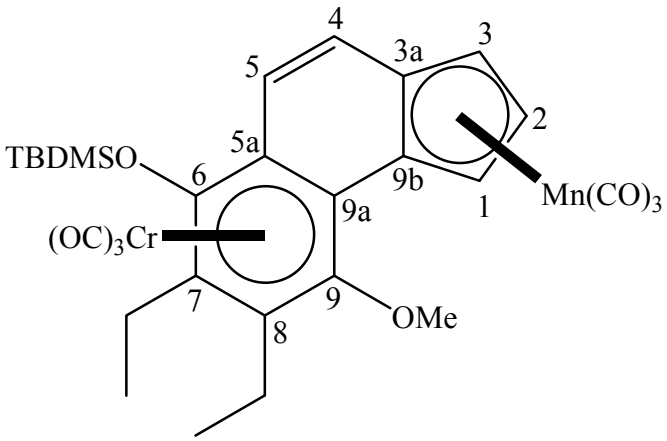
IR (petroleum ether): ν(CO) 2025 (s), 1963 (A1, vs), 1948 (vs), 1901 (E, m), 1890 (E, m) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.25 (3H, s, $SiCH_3$), 0.29 (3H, s, $SiCH_3$), 1.04 (9H, s, $SiC(CH_3)_3$), 1.30-1.32 (6H, m, $CH_2\mathit{CH_3}$, $CH_2\mathit{CH_3}$), 2.39-2.88 (4H, m, $\mathit{CH_2}CH_3$, $\mathit{CH_2}CH_3$), 3.94 (3H, s, OCH_3), 5.01 (1H, s_{br}, CpH), 5.24 (1H, s_{br}, CpH), 5.78 (1H, s_{br}, CpH), 6.97 (1H, d, ^3J= 8.9 Hz, H4 or H5), 7.30 (1H, d, ^3J= 8.9 Hz, H4 or H5).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -2.8 ($SiCH_3$), -2.6 ($SiCH_3$), 15.0 ($CH_2\mathit{CH_3}$), 18.3 ($CH_2\mathit{CH_3}$), 19.0 ($SiC(CH_3)_3$), 19.9 ($\mathit{CH_2}CH_3$), 21.4 ($\mathit{CH_2}CH_3$), 26.0 ($SiC\mathit{(CH_3)_3}$), 67.3 (OCH_3), 77.3 (C2), 79.6, 85.7 (C1, C3), 88.6, 92.6, 101.3, 101.7, 104.2, 113.1 (6 ArC), 120.4, 125.3 (C4 and C5), 128.7, 136.6 (2 ArC), 224.9 ($Mn(CO_3)$), 234.0 ($Cr(CO_3)$).

MS (EI): *m/z* 656.1 [M^+, 4.5], 572.1 [M^+ -3CO, 13.5], 520.2 [M^+ -3CO -Cr, 14], 488.1 [M^+ -6CO, 17], 436.2 [M^+ -6CO -Cr, 99], 382 [M^+ -6CO -Cr -Mn, 4].

***Syn*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-9-methoxy-6-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9b]}manganese (10)**



$C_{30}H_{33}CrMnO_8Si$
Mol. Wt.: 656,60

Yield: 14.5%.
R_f: 0.33 (PE/DCM 3:1).
m.p.: 150°C.

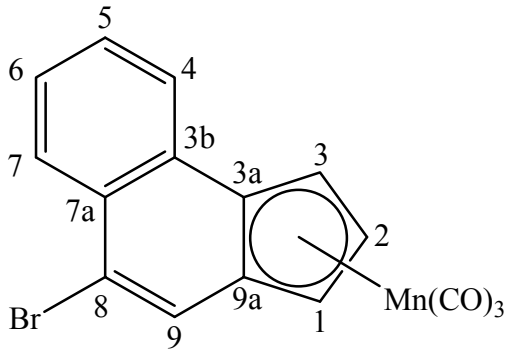
IR (petroleum ether): ν(CO) 2026 (s), 1970 (s), 1950 (s), 1912 (m), 1900 (m) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.25 (3H, s, $SiCH_3$), 0.29 (3H, s, $SiCH_3$), 1.05 (9H, s, $SiC(CH_3)_3$), 1.30-1.32 (6H, m, CH_2CH_3, CH_2CH_3), 2.39-2.89 (4H, m, CH_2CH_3 ,CH_2CH_3), 3.95 (3H, s, OCH_3), 5.01 (1H, s_{br}, CpH), 5.24 (1H, s_{br}, CpH), 5.79 (1H, s_{br}, CpH), 6.98 (1H, d, ^3J= 9.3 Hz, H4 or H5), 7.31 (1H, d, ^3J= 9.3 Hz, H4 or H5).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -2.8 ($SiCH_3$), -2.6 ($SiCH_3$), 15.0 (CH_2CH_3), 18.3 (CH_2CH_3), 19.0 ($SiC(CH_3)_3$), 19.9 (CH_2CH_3), 21.4 (CH_2CH_3), 26.0 ($SiC(CH_3)_3$), 67.3 (OCH_3), 77.3 (C2), 79.6, 85.7 (C1, C3), 88.6, 92.6, 101.3, 101.7, 104.2, 113.1 (6 ArC), 120.4, 125.3 (C4 and C5), 128.7, 136.6 (2 ArC), 224.9 ($Mn(CO_3)$), 234.0 ($Cr(CO_3)$).

MS (EI): *m/z* 656.1 [M^+, 2], 572.1 [M^+ -3CO, 15], 520.2 [M^+ -3CO -Cr, 12], 488.1 [M^+ -6CO, 21], 436.2 [M^+ -6CO -Cr, 99], 382 [M^+ -6CO -Cr -Mn, 2].

Tricarbonyl-{ŋ^5-1,2,3,3a,9a-(8-bromobenzo[*e*]indenyl)}manganese (15)



$C_{16}H_8BrMnO_3$
Mol. Wt.: 383,075 g/mol

KH (1.32 g, 33.0 mmol) is added to a solution of 8-bromobenz[e]-1*H*-indene (7.8 g, 31.8 mmol) in 50 mL of freshly distilled absolute THF and stirred for one hour at room temperature under argon. Then $BrMn(CO)_5$ (9.07 g, 33.0 mmol) is charged in the shlenk tube and the reaction is stirred overnight at room temperature. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3:1) affords 4.87 g of complex **15** (40%) as an air-sensitive yellow product.

Yield: 40%.
R_f: 0.55 (PE/DCM 3:1).
m.p.: 144°C.

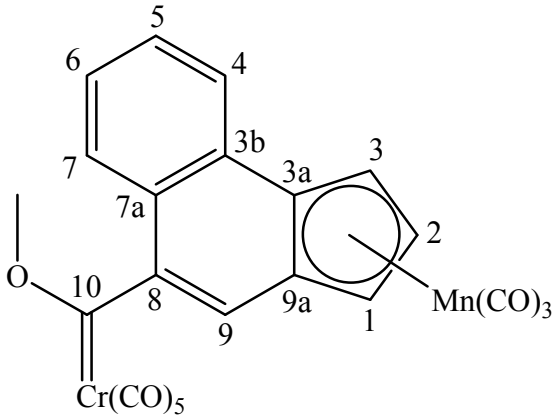
IR (petroleum ether): ν(CO) 2025 (s), 1946 (vs) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 5.09 (1H, pt, ^3J=2.8 Hz, CpH), 5.22 (1H, dd, ^3J= 2.8 Hz, ^3J= 2.8 Hz, CpH), 5.61 (1H, pt, ^3J= 2.8 Hz, CpH), 7.66-7.73 (2H, m, ArH), 7.71 (1H, s_{br}, ArH), 8.02 (1H, m, ArH), 8.25 (1H, m, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ = 72.1, 73.8, 86.9 (C1-C3), 99.0, 101.1 (C3a, C9a), 122.9 (ArC), 123.9, 125.6, 128.3, 129.2, 129.4 (C4-C7, C9), 130.0, 130.1 (2 ArC), 224.9 ($Mn(CO)_3$).

MS (FAB): *m/z* 382 [M^+, 25], 325.9 [M^+ -2CO, 59], 297.9 [M^+ -3CO, 52], 245 [M^+ -Mn -3CO, 42].

Tricarbonyl-{pentacarbonyl[8-benzo[*e*]indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,9a]}manganese (16)



$C_{23}H_{11}CrMnO_9$
Mol. Wt.: 538,26 g/mol

The tricarbonyl-{ŋ^5-1,2,3,3a,9a-(8-bromobenzo[*e*]indenyl)}manganese complex **15** (3.97 g, 10.36 mmol) is dissolved in 80 mL of freshly distilled absolute THF to give a yellow solution. At -78°C is added drop by drop *n*-BuLi, a 2.5 M solution in hexane (4.4 mL, 11.0 mmol), the solution becomes immediately brown, and 5 minutes later $Cr(CO)_6$ (2.64 g, 12.0 mmol) is added. The solution is allowed to reach 20°C within an hour and then the solvent is evaporated via a vacuum pump. The resulting brown oil is then dissolved in 100 mL of absolute DCM and cooled down to -50°C. Methyltriflate (3.28 g, 20.0 mmol) is added drop by drop to the solution which is then warmed to room temperature within half an hour and stirred an extra hour. The solution becomes deep dark red. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3:1) affords 2.83 g (5.26 mmol) of complex **16** as an air-sensitive dark red product.

Yield: 50%.
R_f: 0.36 (PE/DCM 3:1).
m.p.: decomposition.

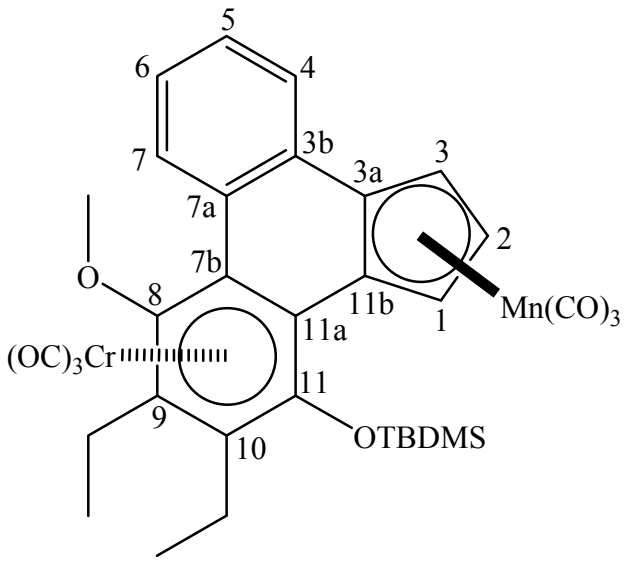
IR (petroleum ether): ν(CO) 2067 (A1, m), 2025 (s), 1957 (E, vs), 1944 (s) cm^{-1}.

^{1}H-NMR (500 MHz, aceton): δ (ppm) 4.34 (3H, s, OCH_3), 5.39 (1H, dd, ^{3}J= 2.7 Hz, ^{3}J= 2.9 Hz, CpH), 5.63 (1H, s_{br}, CpH), 6.00 (1H, s_{br}, CpH), 7.15 (1H, s_{br}, ArH), 7.45 (1H, d, ^{3}J= 8.0 Hz, ArH), 7.66 (1H, m, ArH), 7.73 (1H, m, ArH), 8.32 (1H, d, ^{3}J= 8.0 Hz, ArH).

^{13}C-NMR (125 MHz, CH_2Cl_2): δ (ppm) 66.6 (OCH_3), 75.4 (C1 and C3), 87.8 (C2), 98.7 (ArC), 114.6, 124.8 (2 ArCH), 125.0 (ArC), 126.3, 128.3, 129.0 (3 ArCH), 129.4 (ArC), 216.2 ($Cr(CO)_5$), 224.9 ($Cr(CO)_5$ and $Mn(CO)_3$), 356.7 (C10).

MS (EI): *m/z* 537.8 [M$^+$, 2], 481.9 [M$^+$-2CO, 13], 453.9 [M$^+$-3CO, 3], 425.9 [M$^+$-4CO, 18], 397.9 [M$^+$-5CO, 82], 369.9 [M$^+$-6CO, 8], 341.9 [M$^+$-7CO, 28], 313.9 [M$^+$-8CO, 53].

***Anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (17)**



$C_{34}H_{35}CrMnO_8Si$
Mol. Wt.: 706,66 g/mol

A solution of the tricarbonyl-{pentacarbonyl[8-bromobenzo[*e*]indenyl-(methoxy)carbene] chromium[ŋ^5-1,2,3,3a,9a]}manganese complex **16** (2.45 g, 4.55 mmol) and 3-hexyne (1.50 g, 18.2 mmol) in 50 mL *tert*-butyl-methylether is warmed to 65°C (oil bath temperature) for two hours. Then the phenolic group is protected at room temperature by addition of triethylamine (1.18 g, 18.2 mmol) and *tert*-butyl-dimethylsilyl triflate (4.81 g, 18.2 mmol). After stirring for two hours, chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3/2) affords first 1.65 g of anti complex **17** (51%) followed by 0.68 g of syn complex **18** (21%) as air-sensitive red products. Recrystallisation from dichloromethane at 4°C produces crystals suitable for X-ray analysis.

Yield: 51%.
R_f: 0.68 (PE/DCM 1:1).
m.p.: 92°C.

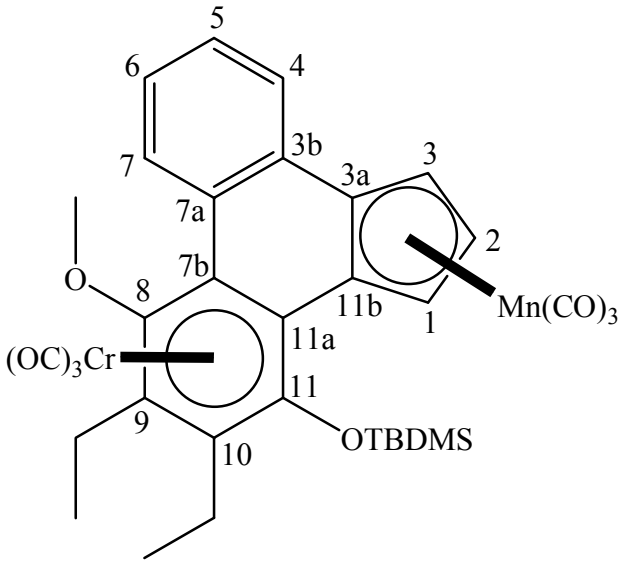
IR (petroleum ether): ν(CO) 2025 (s), 1963 (A1, vs), 1948 (s), 1903 (E, s), 1888 (E, s) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.40 (3H, s, $SiCH_3$), 0.63 (3H, s, $SiCH_3$), 1.17 (9H, s, $SiC(CH_3)_3$), 1.30-1.36 (6H, m, CH_2CH_3, CH_2CH_3), 2.52 (2H, q, ^3J= 7.4 Hz, CH_2CH_3), 2.64 (1H, m, CH_2CH_3), 3.02 (1H, m, CH_2CH_3), 3.57 (3H, s, OCH_3), 5.04 (1H, s_{br}, H1 or H3), 5.60 (1H, s_{br}, H2), 6.19 (1H, s_{br}, H1 or H3), 7.51 (1H, pt, ^3J= 7.5 Hz, H6), 7.60 (1H, pt, ^3J= 8.3 Hz, H5), 7.83 (1H, d, ^3J= 7.5 Hz, H7), 9.01 (1H, d, ^3J= 8.3 Hz, H4).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -2.1 ($SiCH_3$), -0.2 ($SiCH_3$), 15.2 (CH_2CH_3), 18.1 (CH_2CH_3), 19.4 ($SiC(CH_3)_3$), 20.2 (CH_2CH_3), 21.2 (CH_2CH_3), 26.3 ($SiC(CH_3)_3$), 61.7 (OCH_3), 73.8 (C2), 83.9, 84.0 (C1, C3), 86.1, 89.5 (C3a, C11b), 104.3, 105.1, 106.1, 111.7, 120.2 (5 ArC), 123.9 (C7), 126.5 (1 ArC), 128.2 (C6), 128.3 (C4), 129.5 (C5), 130.3 (C3b), 140.7 (1 ArC), 224.4 ($Mn(CO_3)$), 234.1 ($Cr(CO_3)$).

MS (EI): *m/z* 706.1 [M^+, 24], 622.1 [M^+ -3CO, 60], 566.1 [M^+ -5CO, 39], 538.1 [M^+ -6CO, 79], 486.2 [M^+ -6CO -Cr, 64], 425.1 [M^+ -6CO -Cr -Mn, 96].

Syn-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (18)



$C_{34}H_{35}CrMnO_8Si$
Mol. Wt.: 706,66 g/mol

Yield: 21%.
R_f: 0.56 (PE/DCM 1:1).
m.p.: 92°C.

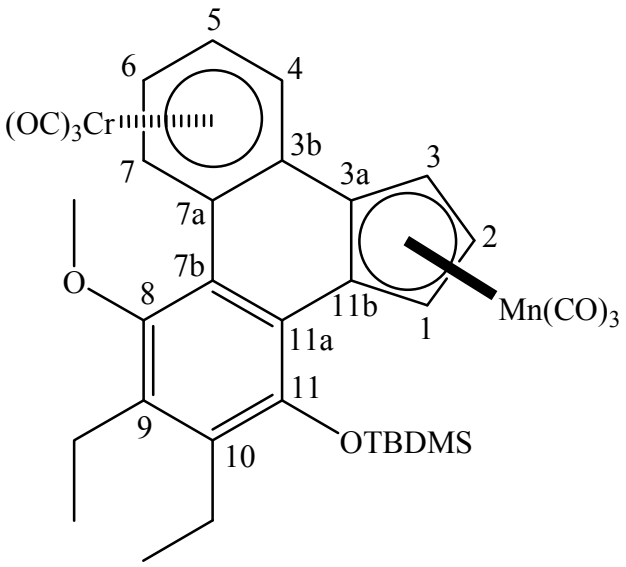
IR (petroleum ether): ν(CO) 2030 (vs), 1967 (A1, s), 1943 (s), 1898 (E, s), 1888 (E, s) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.24 (3H, s, $SiCH_3$), 0.31 (3H, s, $SiCH_3$), 1.03 (9H, s, $SiC(CH_3)_3$), 1.27 (3H, t, ^3J= 7.5 Hz, CH2*CH3*),1.42 (3H, t, ^3J= 7.4 Hz, CH2*CH3*), 2.40 (1H, dt, ^2J=14.8 Hz, ^3J= 7.4 Hz, CH_2CH_3), 2.62 (1H, dt, ^2J=14.8 Hz, ^3J= 7.4 Hz, CH_2CH_3), 2.75 (1H, dt, ^2J=15.0 Hz, ^3J= 7.5 Hz, CH_2CH_3), 3.06 (1H, dt, ^2J=15.0 Hz, ^3J= 7.5 Hz, CH_2CH_3), 3.61 (3H, s, OCH_3), 4.89 (1H, m, CpH), 5.42 (1H, m, CpH), 6.15 (1H, m, CpH), 7.56-7.63 (2H, m, ArH), 7.80 (1H, dd, ^3J= 7.5 Hz, ^3J= 7.8 Hz, ArH), 8.96 (1H, dd, ^3J= 8.0 Hz, ^3J= 7.8 Hz, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -1.3 ($SiCH_3$), -0.3 ($SiCH_3$), 15.2 (CH_2CH_3), 19.2 (CH_2CH_3), 19.4 ($SiC(CH_3)_3$), 20.5 (CH_2CH_3), 21.7 (CH_2CH_3), 26.3 ($SiC(CH_3)_3$), 64.1 (OCH_3), 71.5 (C2), 81.6, 83.2 (C1, C3), 87.3, 100.4, 100.8, 102.4, 112.9 (5 ArC), 123.6, 128.5 (2 ArCH), 128.6, 129.5 (2 ArC), 129.8 (ArCH), 130.2 (ArC), 130.4 (ArCH), 140.6 (ArC), 224.3 ($Mn(CO_3)$), 233.8 ($Cr(CO_3)$).

MS (EI): *m/z* 706.1 [M^+, 2], 622.1 [M^+ -3CO, 5], 570.2 [M^+ -3CO -Cr, 8], 538.1 [M^+ -6CO, 10], 486.2 [M^+ -6CO -Cr, 95], 425.1 [M^+ -6CO -Cr -Mn, 10].

***Anti*-tricarbonyl-{tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (19)**



$C_{34}H_{35}CrMnO_8Si$
Mol. Wt.: 706,66 g/mol

A solution of the *anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese complex **17** (0.72 g, 1.01 mmol) in 100 mL di-*n*-butylether is warmed up to 105°C and stirred for three hours under an argon atmosphere. Chromatography on fine silica gel at 5°C in petroleum ether/dichloromethane (3:2) affords 0.42 g (59%) of complex **19** as an air-sensitive red-orange product. Recrystallisation from dichloromethane at 4°C produces crystals suitable for X-ray analysis.

Yield: 59%.
R_f: 0.6 (PE/DCM 3:2).
m.p.: 149°C.

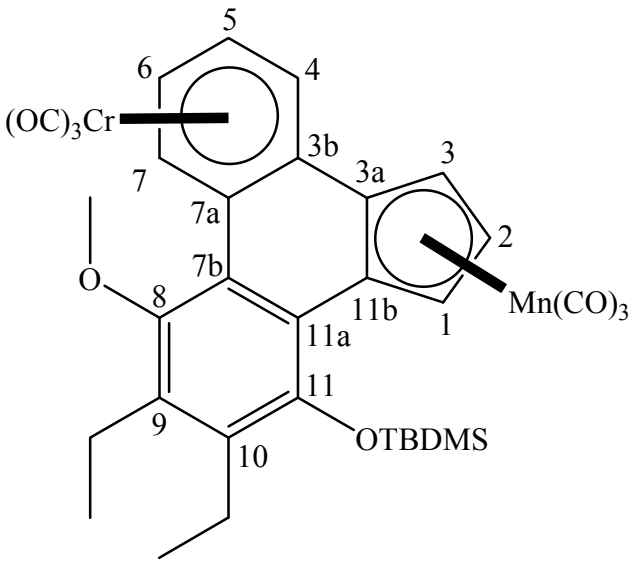
IR (petroleum ether): ν(CO) 2023 (s), 1975 (vs), 1948 (s), 1913 (s) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) -0.09 (3H, s, $SiCH_3$), -0.05 (3H, s, $SiCH_3$), 1.12 (9H, s, $SiC(CH_3)_3$), 1.17-1.23 (6H, m, CH_2CH_3, CH_2CH_3),), 2.57 (1H, dt, ^2J=13.4 Hz, ^3J= 7.3 Hz, CH_2CH_3), 2.68 (1H, dt, ^2J=13.4 Hz, ^3J= 7.3 Hz, CH_2CH_3), 2.84(1H, dt, ^2J=13.3 Hz, ^3J= 7.4 Hz, CH_2CH_3), 2.93 (1H, dt, ^2J=13.3 Hz, ^3J= 7.4 Hz, CH_2CH_3), 3.66 (3H, s, OCH_3), 5.01 (1H, m, CpH), 5.37 (1H, s_{br}, ArH), 5.60 (2H, m, CpH and ArH), 6.05 (2H, m, CpH and ArH), 7.46 (1H, m, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -5.0 ($SiCH_3$), -2.7 ($SiCH_3$), 14.9 (CH_2CH_3), 15.8 (CH_2CH_3), 18.6 ($SiC(CH_3)_3$), 20.6 (CH_2CH_3), 21.2 (CH_2CH_3), 26.2 ($SiC(CH_3)_3$), 62.1 (OCH_3), 72.3 (C2), 81.0, 84.2 (C1, C3), 88.1, 91.8, 92.7, 93.0 (C4-C7), 96.3, 98.0, 98.8, 103.1, 120.2, 120.5, 128.3, 138.5, 146.9, 153.3 (10 ArC), 224.9 ($Mn(CO_3)$), 233.1 ($Cr(CO_3)$).

MS (EI): *m/z* 706.1 [M^+, 4], 622.1 [M^+ -3CO, 10], 570.1 [M^+ -3CO -Cr, 11], 538.1 [M^+ -6CO, 14], 486.1 [M^+ -6CO -Cr, 99], 425.1 [M^+ -6CO -Cr -Mn, 11].

***Syn*-tricarbonyl-{tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (20)**



$C_{34}H_{35}CrMnO_8Si$
Mol. Wt.: 706,66 g/mol

A solution of the *syn*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese complex **18** (0.60 g, 0.85 mmol) in 100 mL di-*n*-butylether is warmed up to 105°C and stirred for three hours under an argon atmosphere. Chromatography on fine silica gel at 5°C in petroleum ether/dichloromethane (3:2) affords 0.38 g (63%) of complex **20** as an air-sensitive red-orange product. Recrystallisation from dichloromethane at 4°C produces crystals suitable for X-ray analysis.

Yield: 63%.
R_f : 0.35 (PE/DCM 3:2).
m.p.: 149°C.

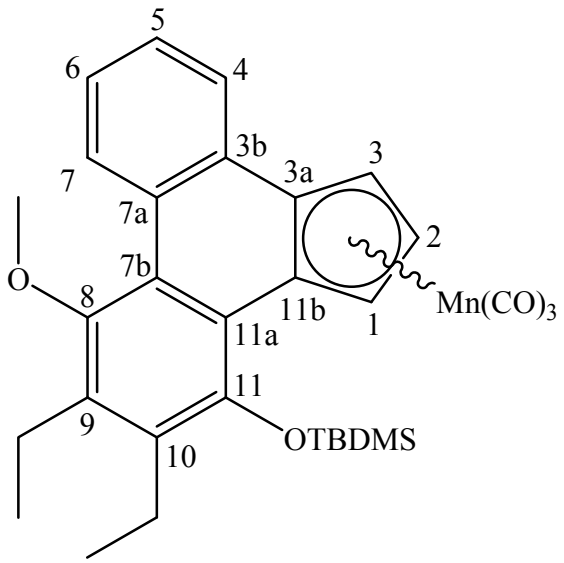
IR (petroleum ether): ν(CO) 2029 (s), 1971 (A1, vs), 1946 (m), 1903 (E, s) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) -0.05 (3H, s, $SiCH_3$), 0.02 (3H, s, $SiCH_3$), 1.12 (3H, t, ^3J= 7.45 Hz, CH_2CH_3), 1.15 (9H, s, $SiC(CH_3)_3$), 1.20 (3H, t, ^3J= 6.9 Hz, CH_2CH_3), 2.57 (1H, m, CH_2CH_3), 2.70 (1H, m, CH_2CH_3), 2.90 (1H, m, CH_2CH_3), 2.98 (1H, m, CH_2CH_3), 4.05 (3H, s, OCH_3), 4.96 (1H, s, CpH), 5.32 (1H, s_{br}, CpH), 5.40 (1H, s_{br}, CpH), 5.58 (1H, m, ArH), 5.75 (1H, s_{br}, ArH), 6.35 (1H, d, ^3J= 6.0 Hz, ArH), 7.54 (1H, d, ^3J= 6.7 Hz, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -4.5 ($SiCH_3$), -2.5 ($SiCH_3$), 14.9 (CH_2CH_3), 15.6 (CH_2CH_3), 18.6 ($SiC(CH_3)_3$), 20.6 (CH_2CH_3), 21.3 (CH_2CH_3), 26.0 ($SiC(CH_3)_3$), 61.9 (OCH_3), 75.7 (C2), 75.9, 84.3 (C1, C3), 87.7, 90.7, 92.2, 95.7 (C4-C7), 94.4, 101.6, 104.1, 104.8, 120.5, 121.7, 139.2, 139.3, 147.6, 153.4 (10 ArC), 224.6 ($Mn(CO_3)$), 233.9 ($Cr(CO_3)$).

MS (EI): *m/z* 706.1 [M^+, 2], 622.1 [M^+ -3CO, 6], 570.1 [M^+ -3CO -Cr, 13], 538.1 [M^+ -6CO, 7], 486.1 [M^+ -6CO -Cr, 99], 425.1 [M^+ -6CO -Cr -Mn, 7].

Tricarbonyl-{ŋ^5-1,2,3,3a,11b-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)}manganese (21)

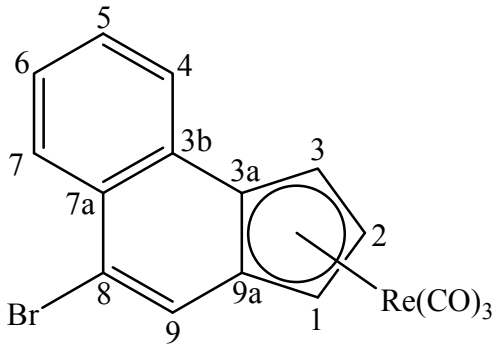


$C_{31}H_{35}MnO_5Si$
Mol. Wt.: 570,63 g/mol

Yield: traces.
R_f: 0.50 (PE/DCM 3:2).

MS(EI): *m/z* 570.2 [M^+, 11], 486.2 [M^+ -3CO, 100].

Tricarbonyl-{ŋ^5-1,2,3,3a,9a-(8-bromobenzo[*e*]indenyl)}rhenium (22)



$C_{16}H_8BrO_3Re$
Mol. Wt.: 514,34 g/mol

KH (0.40 g, 10.0 mmol) was added to a solution of 8-bromobenzo[*e*]-1*H*-indene (2.45 g, 10.0 mmol) in 50 mL of freshly distilled absolute THF and stirred for one hour at room temperature under argon. Then $BrRe(CO)_5$ (4.06 g, 10.0 mmol) is added in the shlenk tube and the reaction is stirred for four hours at reflux of the solvent. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3/1) affords 0.51 g of complex **22** (10%) as an air-sensitive yellow product.

Yield: 10%.
R_f: 0.56 (PE/DCM 3:1).
m.p.: 136°C.

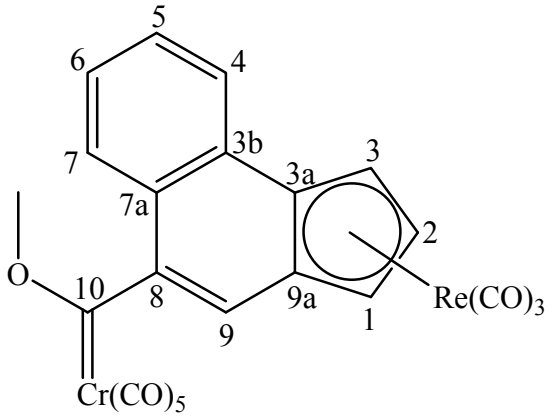
IR (petroleum ether): ν(CO) 2027 (s), 1936 (vs), 1886 (vs) cm^{-1}.

^{1}H-NMR (500 MHz, acetone d6): δ (ppm) 6.03 (1H, dd, ^3J=2.8 Hz, ^3J=2.8 Hz, H2), 6.15 (1H, dd, ^3J= 2.8 Hz, ^4J= 1.6 Hz, H3), 6.68 (1H, ddd, ^3J=2.8 Hz, ^4J=1.6 Hz, ^4J=0.8 Hz, H1), 7.70-7.76 (2H, m, H5 and H6), 8.01 (1H, d, ^{4}J=0.8 Hz, H9), 8.21 (1H, ddd, ^3J=7.4 Hz, ^4J=1.9 Hz, ^5J=0.4 Hz, H4 or H7), 8.29 (1H, ddd, ^3J=7.6 Hz, ^4J=1.5 Hz, ^5J=0.4 Hz, H4 or H7).

^{13}C-NMR (125 MHz, acetone d6): δ (ppm) 72.7, 74.4, 90.0 (C1-C3), 102.8, 104.8 (C3a, C9a), 121.9 (ArC), 123.7, 124.1, 128.2 (3 ArCH), 128.4 (ArC), 128.7 (ArCH), 128.8 (ArC), 129.2 (ArCH), 193.3 ($Re(CO)_3$).

MS (EI): *m/z* 513.9 [M^+, 73], 485.9 [M^+ -1CO, 40], 457.9 [M^+ -2CO, 9], 429.9 [M^+ -3CO, 100].

Tricarbonyl-{pentacarbonyl[8-bromobenzo[*e*]indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,9a]}rhenium (23)



$C_{23}H_{11}CrO_9Re$
Mol. Wt.: 669,53 g/mol

The tricarbonyl-{ŋ^5-1,2,3,3a,9a-(8-bromobenzo[*e*]indenyl)}rhenium complex **22** (0.40 g, 0.78 mmol) is dissolved in 30 mL of freshly distilled absolute THF to give a yellow solution. At -78°C is added drop by drop *n*-BuLi, a 2.5 M solution in hexane (0.31 mL, 0.78 mmol), the solution becomes immediately brown, and five minutes later $Cr(CO)_6$ (0.172 g, 0.78 mmol) is added. The solution is allowed to reach 20°C within an hour and then the solvent is evaporated via a vacuum pump. The resulting brown oil is then dissolved in 30 mL of absolute dichloromethane and cooled down to -50°C. Methyltriflate (0.246 g, 1.5 mmol) is added drop by drop to the solution which is then warmed to room temperature within half an hour and stirred an extra hour. The solution becomes deep dark red. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3:1) affords 0.078 g (0.116 mmol) of complex **23** as an air-sensitive dark red product.

Yield: 15%.
R_f: 0.48 (PE/DCM 3:1).
m.p.: decomposition.

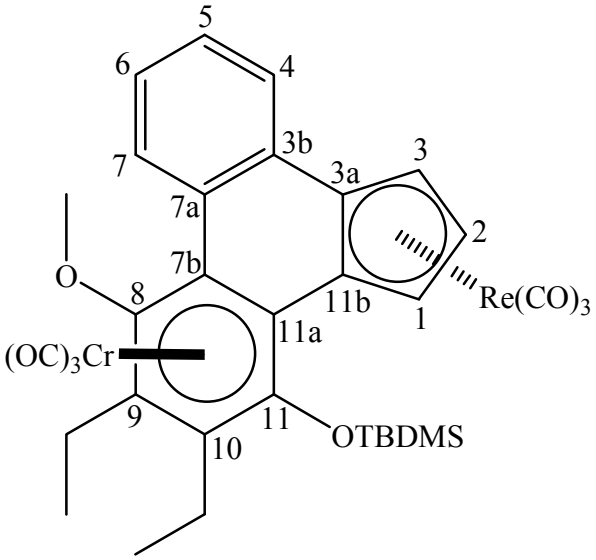
IR (petroleum ether): ν(CO) 2067 (vw), 2011 (s), 1971 (vw), 1936 (m), 1894 (vs) cm^{-1}.

^{1}H-NMR (500 MHz, acetone d6): δ (ppm) 4.17 (3H, s, OCH_3), 5.30 (1H, pt, CpH), 5.78 (1H, pt, ^3J= 2.8 Hz, CpH), 5.90 (1H, m, CpH), 6.93 (1H, s, H9), 7.36 (1H, d, ^3J=8.2 Hz, ArH), 7.56 (1H, m, ArH), 7.65 (1H, m, ArH), 8.07 (1H, d, ^3J=8.1 Hz, ArH).

^{13}C-NMR (125 MHz, acetone d6): δ (ppm) 66.6 (OCH_3), 75.4 (C1 and C3), 90.4 (C2), 112.9, 124.3, 126.3 (3 ArCH), 127.9 (ArC), 128.5, 129.3 (2 ArCH), 193.4 ($Re(CO)_3$), 216.1 (4 *trans*-Cr(CO)), 224.8 (1 *cis*-Cr(CO)), 356.2 (C10).

MS (EI): *m/z* 670.0 [M^+, 39], 614.0 [M^+ -2CO, 10], 586.0 [M^+ -3CO, 3], 558.0 [M^+ -4CO, 20], 530.0 [M^+ -5CO, 100].

***Anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}rhenium (24)**



$C_{34}H_{35}CrO_8ReSi$
Mol. Wt.: 837,92 g/mol

A solution of the carbene complex **23** (0.10 g, 0.15 mmol) and 3-hexyne (0.05 g, 0.60 mmol) in 5 mL *tert*-butyl-methylether is warmed to 65°C (oil bath temperature) for two hours. Then the phenolic group is protected at room temperature by addition of triethylamine (0.06 mL, 0.60 mmol) and *tert*-butyl-dimethylsilyl triflate (0.14 mL, 0.60 mmol). After stirring for two hours, chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (3/2) affords first 0.050 g of anti complex **24** (40%) followed by g 0.012 of syn complex **25** (10%) as air-sensitive orange products. Recrystallisation from dichloromethane at 4°C produces crystals suitable for X-ray analysis.

Yield: 40%.
R_f: 0.62 (PE/DCM 3:1).
m.p.: 156°C.

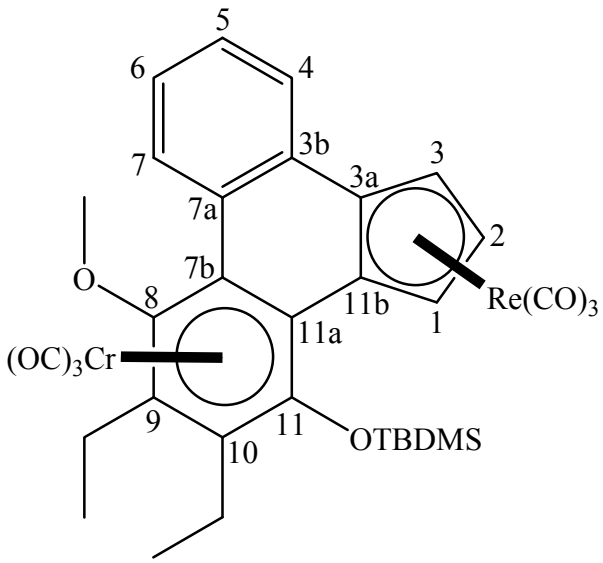
IR (petroleum ether): ν(CO) 2011 (s), 1961 (w), 1892 (vs) 1866 (sh) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) = 0.44 (3H, s, $SiCH_3$), 0.63 (3H, s, $SiCH_3$), 1.15 (9H, s, $SiC(CH_3)_3$), 1.29 (3H, t, ^3J= 7.4 Hz, CH_2CH_3), 1.33 (3H, ^3J= 7.5 Hz, CH_2CH_3), 2.49-2.53 (2H, m, CH_2CH_3), 2.62 (1H, m, CH_2CH_3), 2.98 (1H, m, CH_2CH_3), 3.53 (3H, s, OCH_3), 5.64 (1H, pt, ^3J= 3.0 Hz, H2), 6.24 (1H, dd, ^3J= 3.0 Hz, ^4J= 1.7 Hz, H1 or H3), 6.74 (1H, dd, ^3J= 3.0 Hz, ^4J= 1.7 Hz, H1 or H3), 7.52 (1H, m, ArH), 7.58 (1H, m, ArH), 7.85 (1H, dd, ^3J= 7.6 Hz, ^4J= 1.3 Hz, ArH), 9.01 (1H, dd, ^3J= 8.5 Hz, ^4J= 0.9 Hz, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -2.0 ($SiCH_3$), -0.0 ($SiCH_3$), 15.3 (CH_2CH_3), 18.0 (CH_2CH_3), 19.4 ($SiC(CH_3)_3$), 20.2 (CH_2CH_3), 21.1 (CH_2CH_3), 26.3 ($SiC(CH_3)_3$), 61.8 (OCH_3), 75.1 (C2), 84.9 (C1 or C3), 85.7 (ArC), 86.2 (C1 or C3), 92.5, 103.8, 106.2, 107.5, 111.6, 120.0 (6 ArC), 123.7 (ArCH), 125.0 (ArC), 128.2, 128.4, 129.7 (3 ArCH), 130.1, 140.6 (2 ArC), 193.7 ($Re(CO_3)$), 234.0 ($Cr(CO_3)$).

MS (EI): *m/z* 838.1 [M^+, 13], 754.1 [M^+ -3CO, 100], 702.1 [M^+ -3CO -Cr, 28].

***Syn*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}rhenium (25)**



$C_{34}H_{35}CrO_8ReSi$
Mol. Wt.: 837,92 g/mol

Yield: 10%.
R_f: 0.42 (PE/DCM 3:1).
m.p.: 141°C.

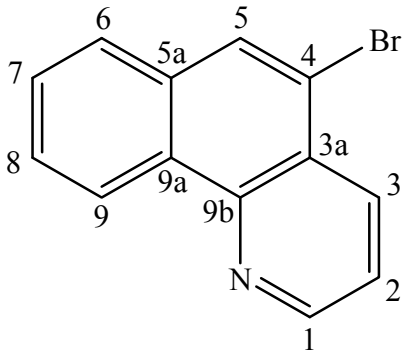
IR (petroleum ether): ν(CO) 2009 (s), 1961 (w), 1892 (vs) 1866 (sh) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) 0.25 (3H, s, $SiCH_3$), 0.29 (3H, s, $SiCH_3$), 1.05 (9H, s, $SiC(CH_3)_3$), 1.27 (3H, t, ^3J= 7.4 Hz, CH_2CH_3), 1.40 (3H, t, ^3J= 7.5 Hz, CH_2CH_3), 2.39 (1H, m, CH_2CH_3), 2.60 (1H, m, CH_2CH_3), 2.72 (1H, m, CH_2CH_3), 3.01 (1H, m, CH_2CH_3), 3.64 (3H, s, OCH_3), 5.56 (1H, s_{br}, CpH), 6.01 (1H, s_{br}, CpH), 6.72 (1H, s_{br}, CpH), 7.58 (1H, pt, ^3J= 8.1 Hz, ArH), 7.63 (1H, pt, ^3J= 7.2 Hz, ArH), 7.81 (1H, d, ^3J= 7.2 Hz, ArH), 9.00 (1H, d, ^3J= 8.1 Hz, ArH).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -1.4 ($SiCH_3$), -0.3 ($SiCH_3$), 15.2 (CH_2CH_3), 19.2 (CH_2CH_3), 19.3 ($SiC(CH_3)_3$), 20.4 (CH_2CH_3), 21.7 (CH_2CH_3), 26.2 ($SiC(CH_3)_3$), 64.5 (OCH_3), 72.2 (C2), 83.7, 85.1 (C1, C3), 90.4, 102.3, 104.7, 112.9 (4 ArC), 123.5(ArCH), 127.7, 128.2 (2ArC), 128.9 (ArCH), 129.6 (ArC), 129.9, 130.5 (2 ArCH), 140.1 (ArC), 193.5 ($Re(CO_3)$), 233.7 ($Cr(CO_3)$)..

MS (EI): *m/z* 838.1 [M^+, 57], 754.1 [M^+ -3CO, 100], 702.1 [M^+ -3CO -Cr, 86].

4-bromobenzo[*h*]quinoline (28)



$C_{13}H_8BrN$
Mol. Wt.: 258,11 g/mol

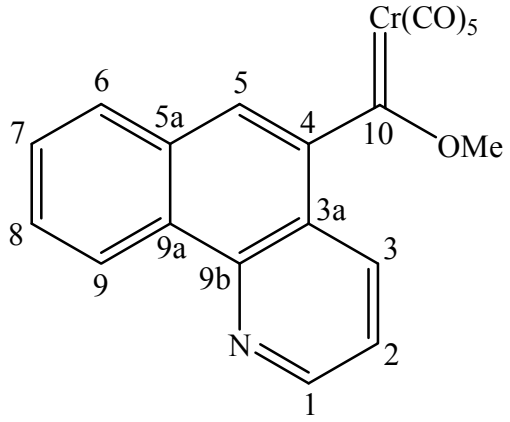
Concentrated H_2SO_4 (50 mL) is poured in a coolable shlenk tube under argon and cooled down to 0°C, then benzo[h]quinoline (5.0 g, 27.9 mmol) is slowly added to the acid, the reaction is very exothermic and should not reach more than 30°C. The solution is cooled down to -26°C and N-bromosuccinimid is slowly added to it, taking care that the temperature stays between -26°C and -22°C. The suspension is stirred at -22°C for one hour and then at -18°C for one hour and a half. The mixture is then poured on 250 g of crashed ice and a 25% ammoniac solution is added until pH=9 is reached, the temperature being kept under 25°C. The mixture is extracted with Et_2O. The organic phase is washed once with a 15% NaOH solution, twice with distilled water and dried over $MgSO_4$. The compound **28** is then purified by crystallisation: dissolved in 100 mL of petroleum ether and 10 mL of dichloromethane and placed in the fridge to produce 5.5 g of small yellow needles (not suitable enough for X-ray).

Yield: 77%.
R_f: 0.76 (DCM/EE 10:1).
m.p.: 104°C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.60 (1H, dd, ^3J= 4.3 Hz, ^3J= 8.2 Hz, H2), 7.68 (1H, ddd, ^3J= 7.0 Hz, ^3J= 8.0 Hz, ^4J= 1.4 Hz, H7), 7.75 (1H, ddd, ^3J= 7.9 Hz, ^3J= 7.0 Hz, ^4J= 1.3 Hz, H8), 7.80 (1H, ddd, ^3J= 7.9 Hz, ^4J= 1.4 Hz, ^5J= 0.7 Hz, H9), 8.12 (1H, s, H5), 8.58 (1H, dd, ^3J= 8.2 Hz, ^4J= 1.7 Hz, H3), 8.99 (1H, dd, ^3J= 4.3 Hz, ^4J= 1.7 Hz, H1), 9.25 (1H, ddd, ^3J= 8.0 Hz, ^4J= 1.3 Hz, ^5J= 0.7 Hz, H6).

^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) 120.3 (C4), 123.2 (C2), 125.4 (C9), 126.3 (ArC), 127.7 (C6), 128.2, 129.6 (C7, C8), 131.6 (C5), 131.7, 134.3 (2 ArC), 136.3 (C3), 147.8 (C9b), 150.0 (C1).

Pentacarbonyl[4-benzo[*h*]quinolyl-(methoxy)carbene]chromium(0) (29)



$C_{20}H_{11}CrNO_6$
Mol. Wt.: 413,30 g/mol

The 4-bromobenzo[*h*]quinoline **27** (1.29 g, 5.0 mmol) is dissolved in 30 mL of freshly distilled absolute tetrahydrofuran to give a yellow solution. At -78°C is added drop by drop *n*-BuLi, a 2.5 M solution in hexane (2.0 mL, 5.0 mmol), the solution becomes immediately brown, and five minutes later $Cr(CO)_6$ (1.10 g, 5.0 mmol) is added. The solution is allowed to reach 20°C within an hour and then the solvent is evaporated via a vacuum pump. The resulting brown oil is then dissolved in 30 mL of absolute dichloromethane and cooled down to -50°C. Methyltriflate (0.82 g, 5.0 mmol) is added slowly to the solution which is then warmed to room temperature within half an hour and stirred an extra hour. The solution becomes deep dark red. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (1:1) affords 1.10 g (2.66 mmol) of complex **29** as an air-sensitive dark red product. Crystallisation from dichloromethane at 4°C produces dark red crystals suitable for X-ray analysis.

Yield: 53%.
R_f: 0.36 (PE/DCM 1:1).
m.p.: decomposition.

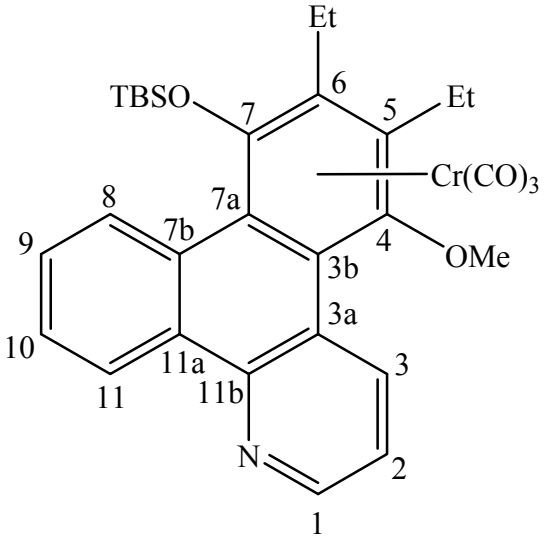
IR (petroleum ether): ν(CO) 2065 (A1, m), 1957 (E, vs) cm^{-1}.

^{1}H-NMR (500 MHz, aceton-d6): δ (ppm) 4.48 (3H, s, O*CH*$_3$), 7.62 (1H, s, H5), 7.71 (1H, dd, ^3J= 8.3 Hz, ^3J= 4.3 Hz, H2), 7.80 (2H, m, H7 and H8), 8.03 (1H, dd, ^3J= 8.3 Hz, ^4J= 1.5 Hz, H3), 8.09 (1H, dd, ^3J= 5.1 Hz, ^4J= 1.8 Hz, H9), 9.07 (1H, dd, ^3J= 4.3 Hz, ^4J= 1.5 Hz, H1), 9.32 (1H, m, H6).

^{13}C-NMR (125 MHz, aceton-d6): δ (ppm) 67.1 (OCH_3), 119.7 (C4), 122.3, 124.2, 127.7, 128.5, 128.8 (5 ArCH), 130.8, 131.9, 132.4 (3 ArC), 145.6 (C9b) 149.5 (C1), 215.7 (4 *trans*-Cr(CO)), 224.5 (1 *cis*-Cr(CO)), 356.8 (C10).

MS (EI): *m/z* 413 [M^+, 3], 385 [M^+ -1CO, 14], 357 [M^+ -2CO, 7],329 [M^+ -3CO, 6],301 [M^+ -4CO, 24], 273 [M^+ -5CO, 99].

Tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline)chromium(0) (30)



$C_{31}H_{35}CrNO_5Si$
Mol. Wt.: 581,69 g/mol

A solution of the pentacarbonyl[4-benzo[*h*]quinolyl-(methoxy)carbene]chromium(0) complex **29** (0.40 g, 0.97 mmol) and 3-hexyne (0.318 g, 3.88 mmol) in 15 mL *tert*-butyl-methylether is warmed up to 65°C (oil bath temperature) for two hours. Then the phenolic group is protected at room temperature by addition of triethylamine (0.36 mL, 4.0 mmol) and *tert*-butyl-dimethylsilyl triflate (1.05 g, 4.0 mmol). After stirring for two hours, chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (1/1) affords 0.23 g of complex **30** as an air-sensitive red product. Crystallisation from dichloromethane at 4°C produces dark red crystals suitable for X-ray analysis.

Yield: 40%.
R_f: 0.37 (PE/DCM 1:1).
m.p.: up to 230°C.

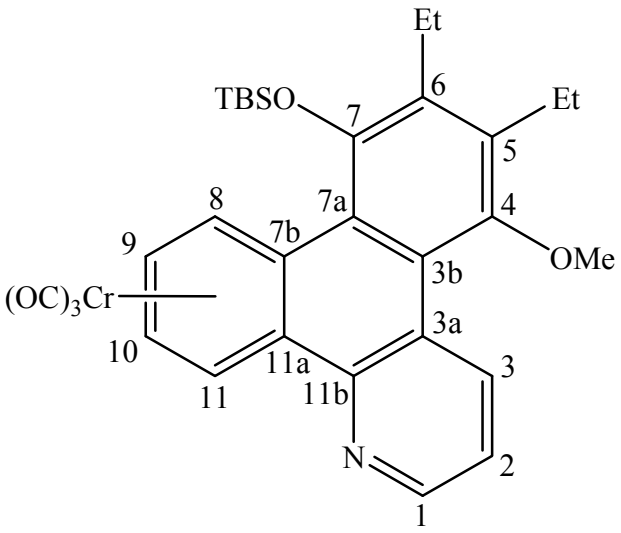
IR (petroleum ether): ν(CO) 1961(A1, vs), 1903 (E, s), 1886 (E, s) cm^{-1}.

^{1}H-NMR (500 MHz, acetone-d6): δ (ppm) -0.65 (3H, s, Si*CH*$_3$), -0.23 (3H, s, Si*CH*$_3$), 0.82 (9H, s, SiC*(CH*$_3$*)*$_3$), 1.06-1.12 (6H, m, CH_2*CH*$_3$, CH_2*CH*$_3$), 2.16-2.23 (1H, m, *CH*$_2$$CH_3$), 2.41-2.51 (2H, m, *CH*$_2$$CH_3$), 2.68-2.75 (1H, m, *CH*$_2$$CH_3$), 3.45 (3H, s, OCH_3), 7.30 (1H, dt, ^{3}*J*= 8.0 Hz, ^{4}*J*= 1.2 Hz, H10), 7.33 (1H, dt, ^{3}*J*= 7.1 Hz, ^{4}*J*= 1.5 Hz, H9), 7.37 (1H, dd, ^{3}*J*= 8.5 Hz, ^{3}*J*= 4.3 Hz, H2), 8.64 (1H, dd, ^{3}*J*= 4.3 Hz, ^{4}*J*= 1.6 Hz, H1), 8.67 (1H, dd, ^{3}*J*= 8.0 Hz, ^{4}*J*= 1.2 Hz, H11), 8.79 (1H, dd, ^{3}*J*= 7.8 Hz, ^{4}*J*= 1.5 Hz, H8), 9.15 (1H, dd, ^{3}*J*= 8.5 Hz, ^{4}*J*= 1.6 Hz, H3).

^{13}C-NMR (125 MHz, acetone-d6): δ (ppm) -4.9, -3.9 ($Si(CH_3)_2$), 14.2 (CH_3), 18.0 (SiC), 18.3 (CH_3), 19.2 (CH_2), 21.3 (CH_2), 25.1 (SiC*(CH*$_3$*)*$_3$), 65.3 (OCH_3), 84.1, 102.0, 105.6, 114.1, 122.2 (5 ArC), 122.6 (C2), 124.9, 127.3, 128.1, 128.2 (C8-C11), 129.3, 129.9, 131.7 (3 ArC), 136.8 (C3), 140.5 (ArC), 148.6 (C11b), 150.2 (C1), 233.5 ($Cr(CO)_3$).

MS (EI): *m/z* 581.2 [M^+, 3], 497.2 [M^+ -3CO, 5], 445.2 [M^+-Cr -3CO, 99].

Tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline)chromium(0) (31)



$C_{31}H_{35}CrNO_5Si$
Mol. Wt.: 581,69 g/mol

A solution of the tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenz[*f*,*h*]quinoline)chromium(0) complex **30** (0.50 g, 0.86 mmol) in 60 mL di-*n*-butylether is warmed up to 105°C and stirred for two hours under an argon atmosphere. Chromatography on fine silica gel at 5°C in only dichloromethane affords 0.45 g of complex **31** (90%) as an air-sensitive red-orange product. Crystallisation from DCM at 4°C produces red crystals suitable for X-ray analysis.

Yield: 90%.
R_f: 0.65 (in DCM).
m.p.: 207°C.

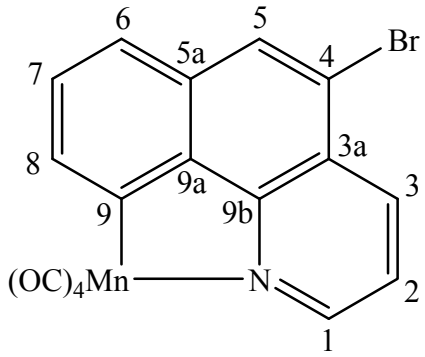
IR (petroleum ether): ν(CO) 1971(A1, vs), 1907 (E, s) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) -0.32 (3H, s, Si*CH*$_3$), -0.13 (3H, s, Si*CH*$_3$), 1.12 (9H, s, SiC*(CH*$_3$*)*$_3$), 1.25-1.29 (6H, m, CH$_2$*CH*$_3$, CH$_2$*CH*$_3$), 2.60-2.67 (1H, m, *CH*$_2$CH$_3$), 2.70-2.77 (1H, m, *CH*$_2$CH$_3$), 2.87-3.00 (2H, m, *CH*$_2$CH$_3$), 3.63 (3H, s, OCH$_3$), 5.59 (1H, dt, ^{3}*J*= 6.7 Hz, ^{4}*J*= 1.0 Hz, H10), 5.64 (1H, dt, ^{3}*J*= 6.0 Hz, ^{4}*J*= 1.3 Hz, H9), 7.42-7.45 (2H, m, H8 and H11), 7.52 (1H, dd, ^{3}*J*= 8.5 Hz, ^{3}*J*= 4.3 Hz, H2), 8.76 (1H, dd, ^{3}J= 4.3 Hz, ^{4}J= 1.5 Hz, H1), 9.51 (1H, dd, ^{3}*J*= 8.5 Hz, ^{4}*J*= 1.5 Hz, H3).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -5.2, -3.0 (Si(CH$_3$)$_2$), 15.0 (CH$_3$), 15.7 (CH$_3$), 18.5 (SiC), 20.5 (CH$_2$), 21.1 (CH$_2$), 26.0 (SiC*(CH*$_3$*)*$_3$), 61.3 (OCH$_3$), 89.5, 91.6, 92.4, 93.2 (C8-C11), 99.2, 107.6, 120.5, 121.9 (4 ArC), 124.0 (C2 or C3), 125.0 (ArC), 135.5 (C2 or C3), 137.6, 138.8, 146.1, 147.2 (4 ArC), 148.1 (C1), 152.6 (C11b), 233.1 (Cr(CO)$_3$).

MS (EI): *m/z* 581.1 [M$^+$, 8], 497.1 [M$^+$ -3CO, 69], 445.2 [M$^+$-Cr -3CO, 66].

Tetracarbonyl{4-bromobenzo[*h*]quinoline-κC^9-κ*N*}manganese(I) (32)



$C_{17}H_7BrMnNO_4$
Mol. Wt.: 424,08 g/mol

The 4-bromobenzo[*h*]quinoline **28** (1.29 g, 5.0 mmol) and the pentacarbonyl-(phenylmethane-κC^1)manganese(I) (1.43 g, 5.0 mmol) are charged in a round bottom flask under argon and then dissolved in absolute *n*-heptane (200 mL). The mixture is stirred and warmed up to the solvent's boiling point (98°C) for two hours. Chromatography on fine silica gel at 10°C with petroleum ether/dichloromethane (3:1) affords 2.08 g (4.9 mmol) of the complex **32** as a yellow powder. Crystallisation from dichloromethane at 4°C produces yellow crystals suitable for X-ray analysis.

Yield: 98%.
R_f: 0.67 (PE/DCM 3:1).
m.p.: 147°C.

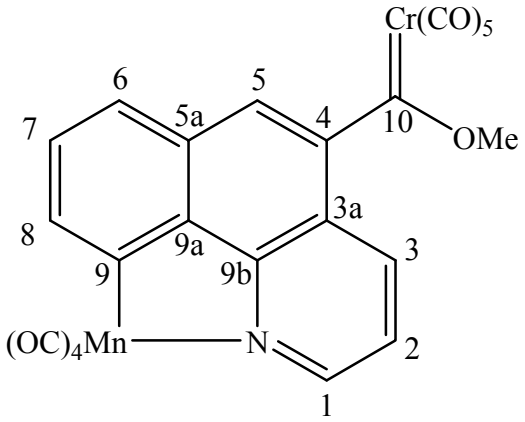
IR (petroleum ether): ν(CO) 2079 (m), 1998 (vs), 1984 (s), 1944 (s) cm^{-1}.

^{1}H-NMR (500 MHz, aceton-d6): δ (ppm) 7.75 (1H, dd, ^3J= 6.8 Hz, ^3J= 7.9 Hz, H7), 7.79 (1H, dd, ^3J= 7.9 Hz, ^4J= 1.1 Hz, H8), 7.90 (1H,dd, ^3J= 8.2 Hz, ^3J= 5.2 Hz, H2), 8.26 (1H, dd, ^3J= 6.8 Hz, ^4J= 1.1 Hz, H6), 8.38 (1H, s, H5), 8.80 (1H, dd, ^3J= 8.2 Hz, ^4J= 1.3 Hz, H3), 9.32 (1H, dd, ^3J= 5.2 Hz, ^4J= 1.3 Hz, H1).

^{13}C-NMR (125 MHz, aceton-d6): δ (ppm) 116.6 (C4) 121.7 (C8) 123.2 (C2) 126.1 (ArC) 130.0 (C7) 132.3 (C5) 133.4 (ArC) 136.8 (C3) 139.4 (C6) 141.5 (ArC) 154.6 (C1) 155.6 (ArC) 171.9 (C9) 213.9, 220.4 ($Mn(CO)_4$).

MS (EI): *m/z* 422.9 [M^+, 7], 338.9 [M^+-3CO, 11], 310.9 [M^+-4CO, 99], 256.9[M^+-Mn -4CO, 54], 177 [M^+-Mn -4CO -Br, 20].

Tetracarbonyl{pentacarbonyl[benzo[*h*]quinolyl-κC^9-κ*N*-4-(methoxy)carbene]chromium(0)}manganese(I) (33)



$C_{24}H_{10}CrMnNO_{10}$
Mol. Wt.: 579,27 g/mol

The pentacarbonyl[4-benzo[*h*]quinolyl-(methoxy)carbene]chromium(0) complex **29** (3.00 g, 7.25 mmol) and the pentacarbonyl-(phenylmethane-κC^1)manganese(I) (2.50 g, 8.74 mmol, 1.2 eq.) are charged in a round bottom flask under argon and then dissolved in absolute *n*-heptane (180 mL). The mixture is then stirred and warmed up to 98°C for two hours. Chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (1:1) affords 3.95 g (6.8 mmol) of the complex **33** as an air-sensitive red powder. Crystallisation from dichloromethane at 4°C produces dark red crystals suitable for X-ray analysis.

Yield: 94%.
R_f: 0.6 (PE/DCM 1:1).
m.p.: decomposition.

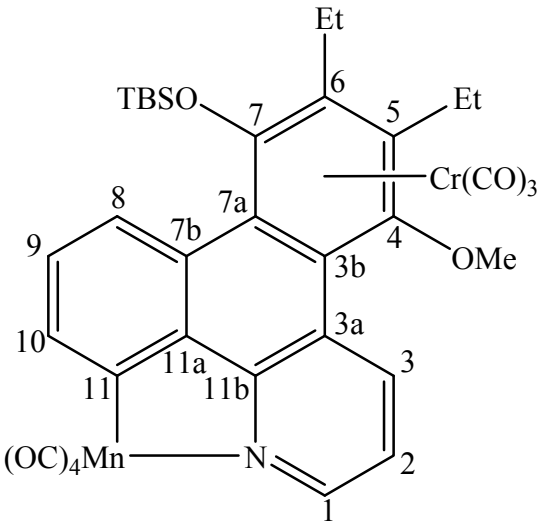
IR (petroleum ether): ν(CO) 2079 (m), 2067 (A1, m), 1996 (vs), 1984 (vs), 1957 (E, s), 1943 (s) cm^{-1}.

^{1}H-NMR (500 MHz, acetone-d6): δ (ppm) 4.62 (3H, s, OCH_3), 7.70 (1H, s, H5), 7.74 (1H, dd, ^3J= 7.2 Hz, ^3J= 7.7 Hz, H7), 7.81 (1H, dd, ^3J= 8.2 Hz, ^3J= 5.0 Hz, H2), 7.86 (1H, d, ^3J= 7.7 Hz, H8), 8.24-8.27 (2H, m, ^3J= 7.2 Hz, ^3J= 8.2 Hz, H3 and H6), 9.30 (1H, d, ^3J= 5.0 Hz, H1).

^{13}C-NMR (125 MHz, acetone-d6): δ (ppm) 122.1 (ArC), 122.8, 122.9, 123.2, 125.6, 128.2, 130.2 (6 ArCH), 132.2, 134.3 (2 ArC), 139.7 (ArCH), 141.3, 152.1 (2 ArC), 154.4 (C1), 154.6 (ArC), 171.9 (C9), 213.8, 213.9 ($Mn(CO)_4$), 215.6 (4 *trans*-Cr(CO)), 220.4 ($Mn(CO)_4$), 224.4 (1 *cis*-Cr(CO)), 355.5 (C10).

MS (EI): *m/z* 578.9 [M^+, 8], 550.9 [M^+ -1CO, 22], 522.9 [M^+ -2CO, 2], 466.9 [M^+ -4CO, 38], 438.9 [M^+ -5CO, 60], 410.9 [M^+ -6CO, 32], 354.9 [M^+ -8CO, 25], 326.9 [M^+ -9CO, 48].

Tetracarbonyl{tricarbonyl(η^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline-κC^{11}-κN)chromium(0)}manganese(I) (34)



$C_{35}H_{34}CrMnNO_9Si$
Mol. Wt.: 747,66 g/mol

A solution of the tetracarbonyl{pentacarbonyl[benzo[*h*]quinolyl-κC^9-κN-4-(methoxy)carbene]chromium(0)}manganese(I) complex **33** (1.80 g, 3.10 mmol) and 3-hexyne (1.02 g, 12.40 mmol) in 35 mL *tert*-butyl-methylether is warmed up to 65°C (oil bath temperature) for two hours. Then the phenolic group is protected at room temperature by addition of triethylamine (0.56 mL, 6.2 mmol) and *tert*-butyl-dimethylsilyl triflate (1.43 mL, 6.2 mmol). After stirring for one hour and a half, chromatography on fine silica gel at 5°C with petroleum ether/dichloromethane (1/1) affords 1.50 g of complex **34** as an air-sensitive red product. Crystallisation from dichloromethane at 4°C produces dark red crystals suitable for X-ray analysis.

Yield: 65%.
R_f: 0.71 (PE/DCM 1:1).
m.p.: 86°C.

IR (petroleum ether): ν(CO) 2079 (m), 2000 (vs), 1983 (vs), 1963 (A1, s), 1942 (s), 1907 (E, m), 1890 (E, m) cm^{-1}.

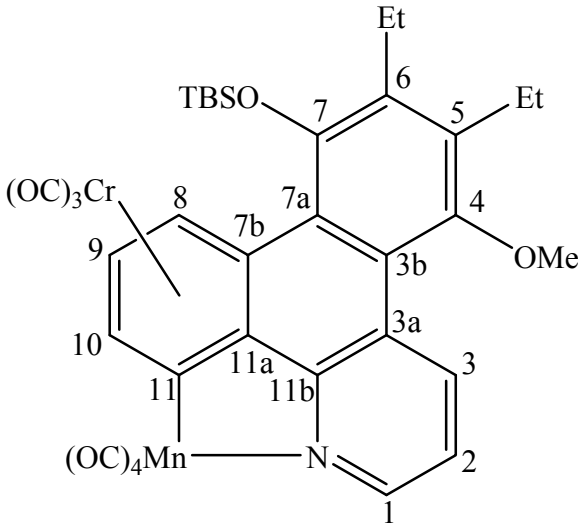
^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) -0.22 (3H, s, Si*CH*$_3$), 0.08 (3H, s, Si*CH*$_3$), 1.18 (9H, s, SiC*(CH*$_3$*)*$_3$), 1.40-1.43 (3H, t, ^3J= 7.45 Hz, CH_2*CH*$_3$), 1.45-1.48 (3H, dt, ^3J= 7.45 Hz, CH_2*CH*$_3$), 2.47 (1H, m, ^3J= 7.35 Hz, *CH*$_2$$CH_3$), 2.72-2.81 (2H, m, *CH*$_2$$CH_3$), 3.02 (1H, m, ^3J= 7.55 Hz, *CH*$_2$$CH_3$), 3.76 (3H, s, OCH_3), 7.50 (1H, dd, ^3J= 8.4 Hz, ^3J= 5.3 Hz, H2), 7.55 (1H, dd, ^3J= 8.2 Hz, ^3J= 7.0 Hz, H9), 8.12 (1H, dd, ^3J= 7.0 Hz, ^4J= 0.9 Hz, H8), 8.68 (1H, dd, ^3J= 8.2 Hz, ^4J= 0.9 Hz, H10), 9.03 (1H, dd, ^3J= 5.3 Hz, ^4J= 1.4 Hz, H3), 9.50 (1H, dd, ^3J= 8.4 Hz, ^4J= 1.4 Hz, H1).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -3.6, -2.9 ($Si(CH_3)_2$), 15.3 (CH_3), 18.9 (SiC), 19.1 (CH_3), 20.1 (CH_2), 21.9 (CH_2), 26.1 (SiC*(CH*$_3$*)*$_3$), 66.2 (OCH_3), 86.3, 99.6, 106.5, 113.7 (4 ArC), 122.7 (C2), 123.9 (C8 or C10), 125.1 (ArC), 129.6 (C9), 131.1, 132.8 (2 ArC), 138.7

(C3), 139.3 (ArC), 140.4 (C8 or C10), 140.5 (ArC), 154.6 (C1), 159.8 (ArC), 173.3 (C11), 213.9, 214.6, 220.7 ($Mn(CO)_4$), 233.9 ($Cr(CO)_3$).

MS (EI): *m/z* 747.2 [M^+, 25], 691.2 [M^+ -2CO, 18], 663.1 [M^+ -3CO, 6], 635.2 [M^+ -4CO, 11], 607.1 [M^+ -5CO, 9], 581.2 [M^+ -6CO, 8], 551.2 [M^+ -7CO, 27], 497.2 [M^+ -7CO -Cr, 99], 445.2 [M^+ -7CO -Cr -Mn, 42].

Tetracarbonyl{tricarbonyl(η^6-7b,8,9,10,11,11a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline-κC^{11}-κ*N*)chromium(0)}manganese(I) (35)



$C_{35}H_{34}CrMnNO_9Si$
Mol. Wt.: 747,66 g/mol

A solution of the heterobimetallic kinetic complex **34** (0.91 g, 1.21 mmol) in 60 mL di-*n*-butylether is warmed up to 105°C and stirred for three hours under an argon atmosphere. Chromatography on fine silica gel at 5°C in only dichloromethane affords 0.47 g of complex **35** as an air-sensitive red-orange product. Crystallisation from dichloromethane at 4°C produces red crystals suitable for X-ray analysis.

Yield: 52%.
R_f: 0.57 (PE/DCM 1:1).
m.p.: 60°C.

IR (petroleum ether): ν(CO) 2085 (m), 2006 (vs), 1988 (s), 1975 (A1, s), 1950 (s) and 1898 (E, m) cm^{-1}.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ (ppm) -0.28 (3H, s, Si*CH*$_3$), -0.12 (3H, s, Si*CH*$_3$), 1.12 (9H, s, SiC*(CH*$_3$*)*$_3$), 1.26 (3H, t, ^{3}J= 7.45 Hz, CH_2*CH*$_3$), 1.27 (3H, t, ^{3}J= 7.35 Hz, CH_2*CH*$_3$), 2.62 (1H, m, *CH*$_2$CH$_3$), 2.72 (1H, m, *CH*$_2$CH$_3$), 2.87-2.99 (2H, m, *CH*$_2$CH$_3$), 3.66 (3H, s, OCH_3), 5.46 (1H, dd, ^{3}*J*= 6.9 Hz, ^{3}*J*= 5.9 Hz, H9), 6.23 (1H, dd, ^{3}*J*= 5.9 Hz, ^{4}*J*= 1.2 Hz, H8), 7.44 (1H, dd, ^{3}*J*= 6.9 Hz, ^{4}*J*= 1.2 Hz, H10), 7.50 (1H, dd, ^{3}*J*= 8.5 Hz, ^{3}*J*= 5.2 Hz, H2), 8.84 (1H, dd, ^{3}*J*= 5.2 Hz, ^{4}*J*= 1.3 Hz, H3), 9.63 (1H, dd, ^{3}*J*= 8.5 Hz, ^{4}*J*= 1.3 Hz, H1).

^{13}C-NMR (125 MHz, CD_2Cl_2): δ (ppm) -5.1, -3.0 ($Si(CH_3)_2$), 14.9 (CH_3), 15.7 (CH_3), 18.5 (SiC), 20.5 (CH_2), 21.2 (CH_2), 26.0 ($SiC(CH_3)_3$), 61.3 (OCH_3), 91.9 (C9), 93.5 (C8 or C10), 104.6 (ArC), 108.0 (C8 or C10), 109.7, 120.2, 121.8 (3 ArC), 124.6 (C2), 127.9, 134.4 (2 ArC), 137.4 (C1), 138.4, 139.0, 147.5 (3 ArC), 152.5 (C3), 153.0, 158.1 (2 ArC), 211.2 211.7, 212.7, 219.6 ($Mn(CO)_4$), 235.4 ($Cr(CO)_3$).

MS (EI): *m/z* 747.1 [M^+, 1], 663.1 [M^+ -3CO, 29], 635.1 [M^+ -4CO, 36], 607.1 [M^+ -5CO, 26], 551.1[M^+ -7CO, 2] 497.2 [M^+, -7CO -Cr, 99], 445.3 [M^+, -7CO -Cr -Mn, 14].

VIII] APPENDIX

1. List of the numbered compounds

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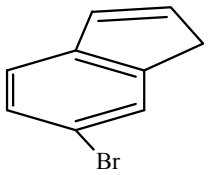

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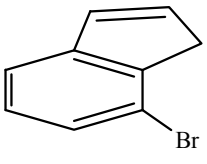

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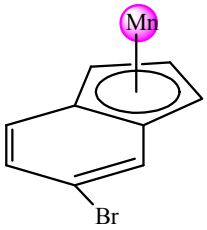

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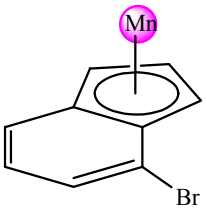

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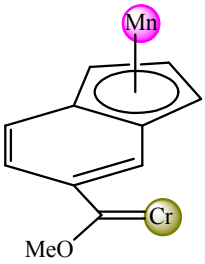

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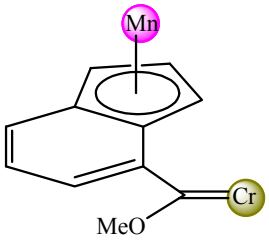

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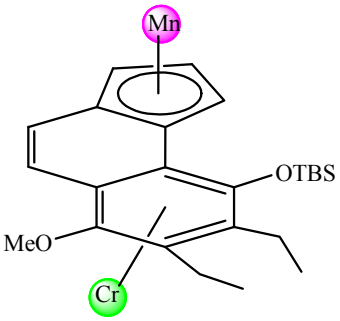

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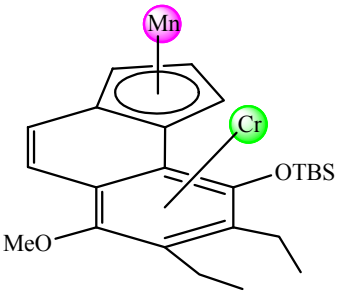

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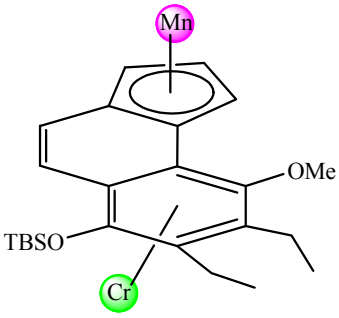

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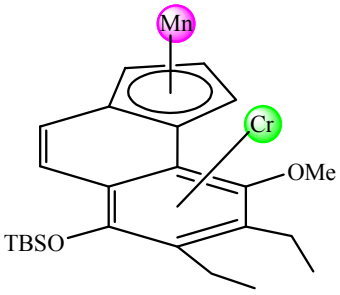

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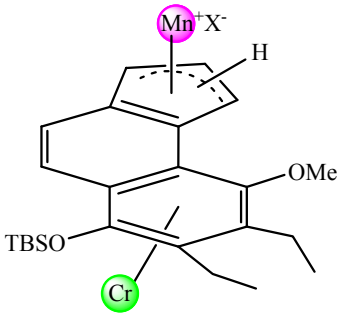

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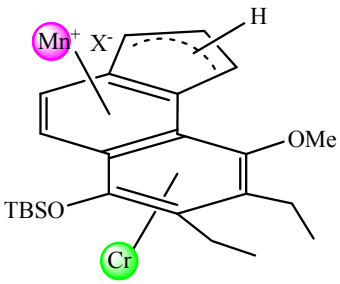

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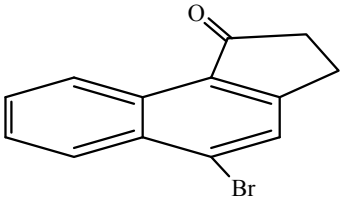

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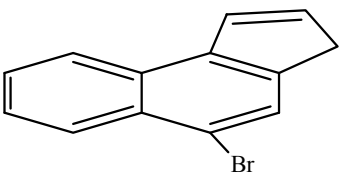

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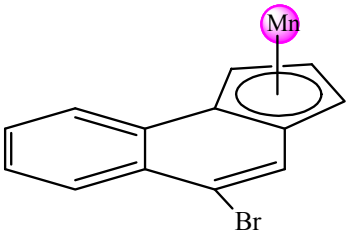

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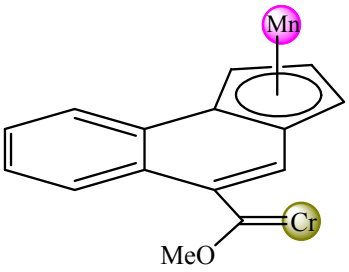

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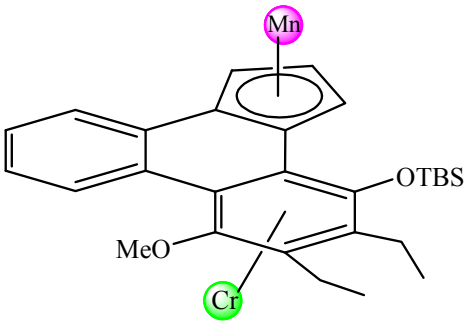

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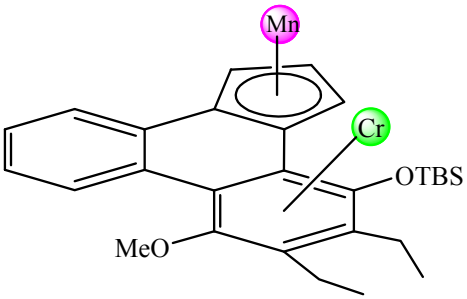

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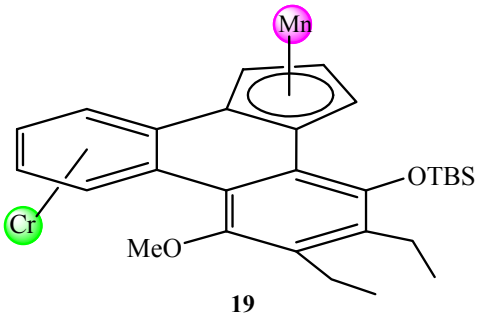

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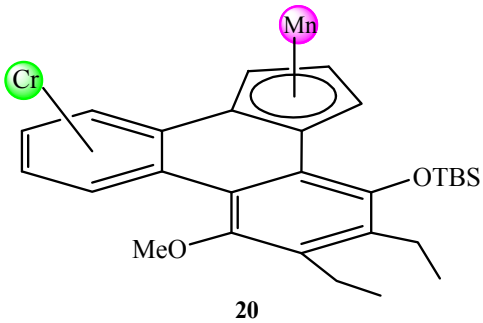

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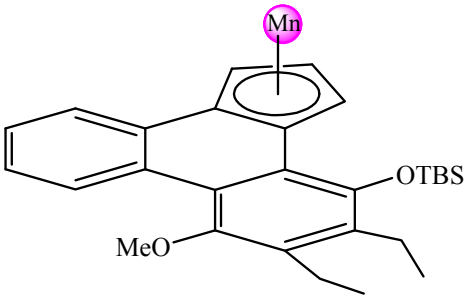

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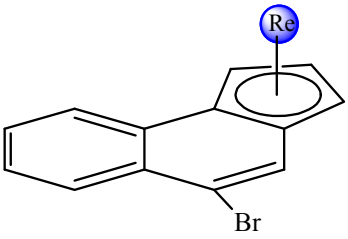

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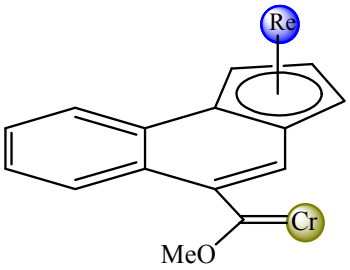

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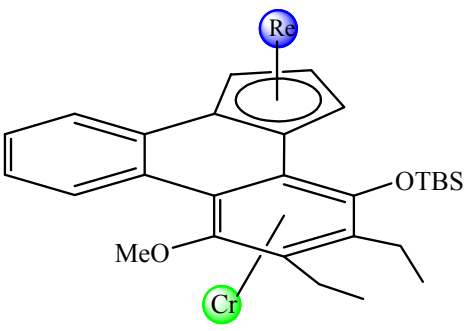

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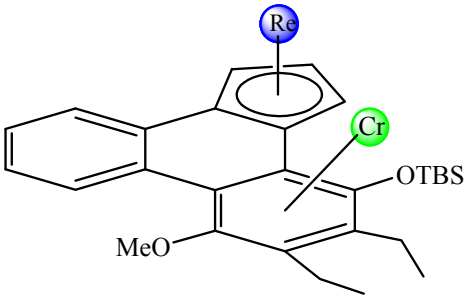

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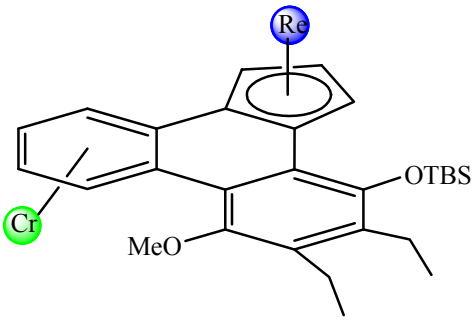

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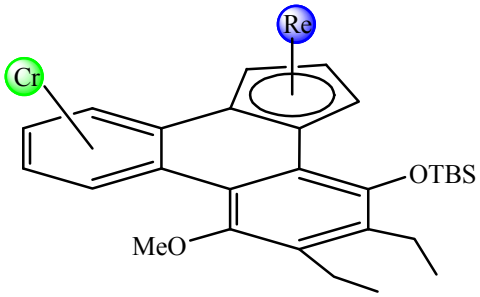

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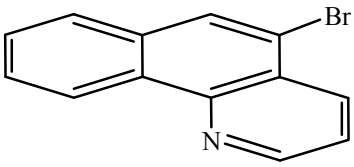

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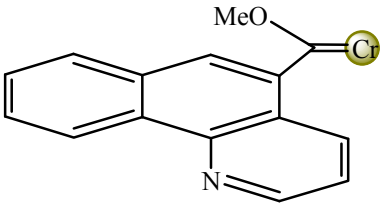

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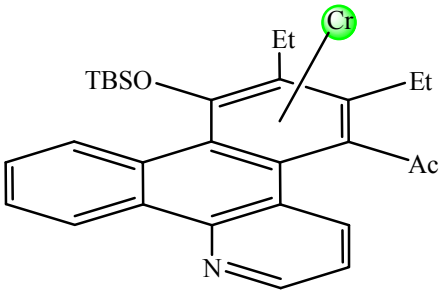

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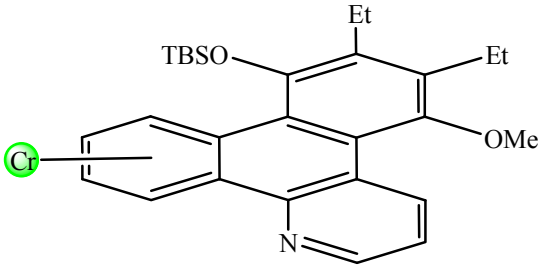

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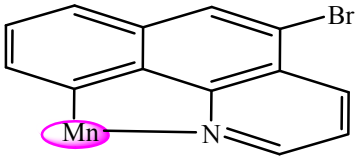

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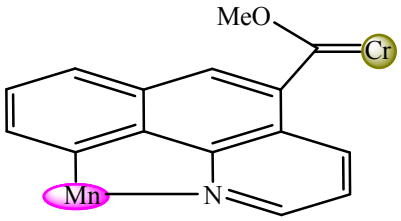

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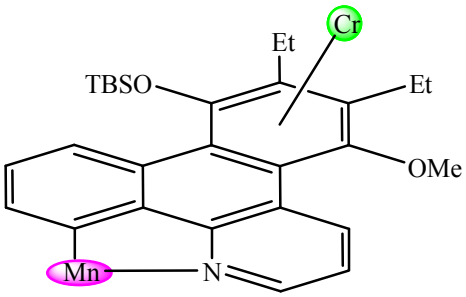

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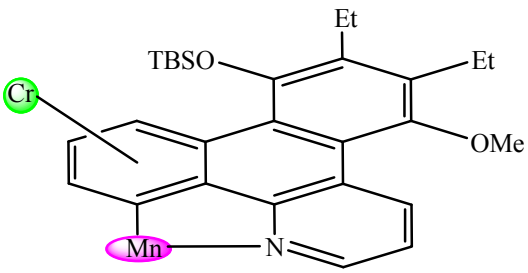


35

2. X-Ray structures analyses of organometallic compounds

2.1 *Anti*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-6-methoxy-9-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9a]}manganese (7)

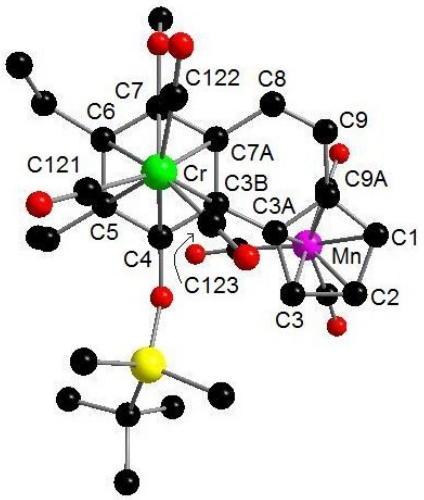


Table 1. Crystal data and structure refinement for **7**.

Empirical formula	C_{30} H_{33} Cr Mn O_8 Si
Formula weight	656.59
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$ (No.14)
Unit cell dimensions	a = 12.6963(1) Å b = 18.5690(2) Å β = 98.947(1)°. c = 13.0998(2) Å
Volume	3050.80(6) Å^3
Z, Calculated density	4, 1.430 Mg/m^3
Absorption coefficient	0.857 mm^{-1}
F(000)	1360
Crystal size	0.30 x 0.30 x 0.20 mm
Theta range for data collection	1.92 to 27.89°.
Limiting indices	-14<=h<=16, -24<=k<=22, -10<=l<=17
Reflections collected / unique	21733 / 7246 [R(int) = 0.0429]
Completeness to theta = 27.89	99.4 %

Max. and min. transmission	0.8473 and 0.7831
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7246 / 0 / 378
Goodness-of-fit on F^2	1.042
Final R indices [I>2σ(I)]	R1 = 0.0355, wR^2 = 0.0898
R indices (all data)	R1 = 0.0498, wR^2 = 0.0968
Largest diff. peak and hole	0.356 and -0.435 eÅ^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **7**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mn	7566(1)	4115(1)	-321(1)	34(1)
Cr	7636(1)	1292(1)	934(1)	23(1)
C(1)	7317(2)	4246(1)	1250(2)	46(1)
C(2)	8406(2)	4269(1)	1196(2)	44(1)
C(3)	8716(2)	3603(1)	789(2)	34(1)
C(3A)	7792(2)	3147(1)	628(1)	29(1)
C(3B)	7605(1)	2419(1)	213(1)	25(1)
C(4)	8406(1)	1989(1)	-151(1)	22(1)
C(5)	8134(1)	1324(1)	-650(1)	24(1)
C(6)	7067(1)	1054(1)	-748(1)	26(1)
C(7)	6304(1)	1460(1)	-339(1)	27(1)
C(7A)	6545(1)	2149(1)	131(1)	27(1)
C(8)	5716(2)	2562(1)	512(2)	36(1)
C(9)	5887(2)	3235(1)	858(2)	43(1)
C(9A)	6920(2)	3550(1)	914(2)	36(1)
O(41)	9402(1)	2267(1)	-111(1)	27(1)
Si(42)	10638(1)	2139(1)	544(1)	25(1)
C(43)	10847(2)	2676(1)	1757(2)	36(1)
C(44)	10915(2)	1192(1)	952(2)	35(1)
C(45)	11528(1)	2476(1)	-377(2)	30(1)
C(46)	11159(2)	3217(1)	-790(2)	60(1)
C(47)	11531(2)	1966(1)	-1292(2)	50(1)
C(48)	12667(2)	2537(1)	207(2)	49(1)
C(51)	8940(1)	943(1)	-1186(1)	28(1)
C(52)	8795(2)	1158(1)	-2322(2)	38(1)
C(61)	6732(2)	352(1)	-1307(2)	35(1)
C(62)	6484(2)	-267(1)	-622(2)	40(1)
O(71)	5289(1)	1193(1)	-367(1)	33(1)
C(72)	4556(2)	1403(1)	-1269(2)	47(1)
C(111)	6264(2)	4403(1)	-942(2)	55(1)
O(111)	5431(2)	4589(1)	-1308(2)	87(1)
C(112)	8221(2)	4882(1)	-741(2)	52(1)
O(112)	8697(2)	5359(1)	-1010(2)	81(1)
C(113)	7876(2)	3633(1)	-1426(2)	41(1)

O(113)	8127(2)	3318(1)	-2102(1)	58(1)
C(121)	8396(2)	462(1)	1213(1)	31(1)
O(121)	8873(1)	-66(1)	1416(1)	48(1)
C(122)	6647(2)	895(1)	1657(2)	33(1)
O(122)	6038(1)	619(1)	2095(1)	51(1)
C(123)	8360(2)	1646(1)	2154(2)	32(1)
O(123)	8819(1)	1856(1)	2927(1)	51(1)

Table 3. Bond lengths [Å] and angles [°] for **7**.

Mn-C(112)	1.780(2)
Mn-C(113)	1.796(2)
Mn-C(111)	1.806(2)
Mn-C(3)	2.1193(18)
Mn-C(2)	2.124(2)
Mn-C(1)	2.145(2)
Mn-C(3A)	2.1777(17)
Mn-C(9A)	2.192(2)
Cr-C(121)	1.8247(19)
Cr-C(123)	1.836(2)
Cr-C(122)	1.840(2)
Cr-C(7)	2.2047(17)
Cr-C(6)	2.2533(17)
Cr-C(4)	2.2541(16)
Cr-C(7A)	2.2590(17)
Cr-C(5)	2.2626(17)
Cr-C(3B)	2.2945(17)
C(1)-C(2)	1.396(3)
C(1)-C(9A)	1.432(3)
C(2)-C(3)	1.425(3)
C(3)-C(3A)	1.436(3)
C(3A)-C(9A)	1.433(3)
C(3A)-C(3B)	1.463(2)
C(3B)-C(7A)	1.425(2)
C(3B)-C(4)	1.431(2)
C(4)-O(41)	1.3600(19)
C(4)-C(5)	1.415(2)
C(5)-C(6)	1.432(2)
C(5)-C(51)	1.504(2)
C(6)-C(7)	1.398(2)
C(6)-C(61)	1.523(2)
C(7)-O(71)	1.377(2)
C(7)-C(7A)	1.431(3)
C(7A)-C(8)	1.452(2)
C(8)-C(9)	1.336(3)
C(9)-C(9A)	1.427(3)
O(41)-Si(42)	1.6844(12)
Si(42)-C(44)	1.8553(19)
Si(42)-C(43)	1.8602(19)
Si(42)-C(45)	1.8833(19)
C(45)-C(46)	1.525(3)
C(45)-C(47)	1.527(3)
C(45)-C(48)	1.532(3)
C(51)-C(52)	1.525(3)
C(61)-C(62)	1.521(3)
O(71)-C(72)	1.440(2)
C(111)-O(111)	1.144(3)

C(112)-O(112)	1.157(3)
C(113)-O(113)	1.147(3)
C(121)-O(121)	1.162(2)
C(122)-O(122)	1.152(2)
C(123)-O(123)	1.154(2)
C(112)-Mn-C(113)	88.75(10)
C(112)-Mn-C(111)	93.60(11)
C(113)-Mn-C(111)	94.86(11)
C(112)-Mn-C(3)	105.39(9)
C(113)-Mn-C(3)	96.64(9)
C(111)-Mn-C(3)	157.94(10)
C(112)-Mn-C(2)	89.45(9)
C(113)-Mn-C(2)	132.81(9)
C(111)-Mn-C(2)	132.31(11)
C(3)-Mn-C(2)	39.24(7)
C(112)-Mn-C(1)	110.55(10)
C(113)-Mn-C(1)	155.98(8)
C(111)-Mn-C(1)	97.91(11)
C(3)-Mn-C(1)	65.21(8)
C(2)-Mn-C(1)	38.18(9)
C(112)-Mn-C(3A)	144.11(9)
C(113)-Mn-C(3A)	91.33(8)
C(111)-Mn-C(3A)	122.12(9)
C(3)-Mn-C(3A)	39.00(7)
C(2)-Mn-C(3A)	64.80(7)
C(1)-Mn-C(3A)	64.65(7)
C(112)-Mn-C(9A)	149.06(9)
C(113)-Mn-C(9A)	120.71(8)
C(111)-Mn-C(9A)	93.05(10)
C(3)-Mn-C(9A)	64.89(8)
C(2)-Mn-C(9A)	64.18(9)
C(1)-Mn-C(9A)	38.54(8)
C(3A)-Mn-C(9A)	38.29(7)
C(121)-Cr-C(123)	87.16(8)
C(121)-Cr-C(122)	86.57(8)
C(123)-Cr-C(122)	89.14(8)
C(121)-Cr-C(7)	126.24(8)
C(123)-Cr-C(7)	145.91(8)
C(122)-Cr-C(7)	86.65(7)
C(121)-Cr-C(6)	96.30(7)
C(123)-Cr-C(6)	164.16(7)
C(122)-Cr-C(6)	106.47(8)
C(7)-Cr-C(6)	36.54(6)
C(121)-Cr-C(4)	110.10(7)
C(123)-Cr-C(4)	97.80(7)
C(122)-Cr-C(4)	162.14(7)
C(7)-Cr-C(4)	78.37(6)
C(6)-Cr-C(4)	66.47(6)
C(121)-Cr-C(7A)	162.74(8)
C(123)-Cr-C(7A)	109.90(7)
C(122)-Cr-C(7A)	95.96(7)
C(7)-Cr-C(7A)	37.37(7)
C(6)-Cr-C(7A)	66.59(6)
C(4)-Cr-C(7A)	66.21(6)
C(121)-Cr-C(5)	89.52(7)
C(123)-Cr-C(5)	127.99(7)
C(122)-Cr-C(5)	142.44(8)
C(7)-Cr-C(5)	66.01(6)
C(6)-Cr-C(5)	36.98(6)
C(4)-Cr-C(5)	36.51(6)

C(7A)-Cr-C(5)	78.05(6)
C(121)-Cr-C(3B)	145.85(7)
C(123)-Cr-C(3B)	90.33(7)
C(122)-Cr-C(3B)	127.46(7)
C(7)-Cr-C(3B)	66.24(6)
C(6)-Cr-C(3B)	78.12(6)
C(4)-Cr-C(3B)	36.67(6)
C(7A)-Cr-C(3B)	36.47(6)
C(5)-Cr-C(3B)	65.65(6)
C(2)-C(1)-C(9A)	108.38(18)
C(2)-C(1)-Mn	70.11(13)
C(9A)-C(1)-Mn	72.50(12)
C(1)-C(2)-C(3)	109.06(19)
C(1)-C(2)-Mn	71.71(12)
C(3)-C(2)-Mn	70.19(11)
C(2)-C(3)-C(3A)	107.41(19)
C(2)-C(3)-Mn	70.57(11)
C(3A)-C(3)-Mn	72.70(10)
C(9A)-C(3A)-C(3)	107.52(17)
C(9A)-C(3A)-C(3B)	119.47(17)
C(3)-C(3A)-C(3B)	132.95(17)
C(9A)-C(3A)-Mn	71.38(10)
C(3)-C(3A)-Mn	68.30(10)
C(3B)-C(3A)-Mn	123.44(12)
C(7A)-C(3B)-C(4)	119.29(15)
C(7A)-C(3B)-C(3A)	116.78(15)
C(4)-C(3B)-C(3A)	123.86(16)
C(7A)-C(3B)-Cr	70.41(9)
C(4)-C(3B)-Cr	70.13(9)
C(3A)-C(3B)-Cr	134.36(12)
O(41)-C(4)-C(5)	120.52(14)
O(41)-C(4)-C(3B)	118.63(15)
C(5)-C(4)-C(3B)	120.44(15)
O(41)-C(4)-Cr	133.32(11)
C(5)-C(4)-Cr	72.07(9)
C(3B)-C(4)-Cr	73.20(9)
C(4)-C(5)-C(6)	120.41(15)
C(4)-C(5)-C(51)	119.45(15)
C(6)-C(5)-C(51)	119.77(15)
C(4)-C(5)-Cr	71.42(9)
C(6)-C(5)-Cr	71.16(10)
C(51)-C(5)-Cr	136.26(12)
C(7)-C(6)-C(5)	118.59(16)
C(7)-C(6)-C(61)	119.23(16)
C(5)-C(6)-C(61)	122.16(16)
C(7)-C(6)-Cr	69.84(10)
C(5)-C(6)-Cr	71.87(10)
C(61)-C(6)-Cr	131.42(12)
O(71)-C(7)-C(6)	119.74(16)
O(71)-C(7)-C(7A)	118.06(15)
C(6)-C(7)-C(7A)	122.19(16)
O(71)-C(7)-Cr	125.03(11)
C(6)-C(7)-Cr	73.62(10)
C(7A)-C(7)-Cr	73.38(10)
C(3B)-C(7A)-C(7)	118.91(15)
C(3B)-C(7A)-C(8)	120.95(17)
C(7)-C(7A)-C(8)	120.14(16)
C(3B)-C(7A)-Cr	73.12(9)
C(7)-C(7A)-Cr	69.26(9)
C(8)-C(7A)-Cr	129.58(13)

C(9)-C(8)-C(7A)	121.55(19)
C(8)-C(9)-C(9A)	119.97(18)
C(9)-C(9A)-C(1)	131.43(19)
C(9)-C(9A)-C(3A)	120.97(18)
C(1)-C(9A)-C(3A)	107.58(19)
C(9)-C(9A)-Mn	127.13(15)
C(1)-C(9A)-Mn	68.96(12)
C(3A)-C(9A)-Mn	70.33(11)
C(4)-O(41)-Si(42)	138.85(11)
O(41)-Si(42)-C(44)	113.65(8)
O(41)-Si(42)-C(43)	110.90(8)
C(44)-Si(42)-C(43)	105.43(9)
O(41)-Si(42)-C(45)	103.34(7)
C(44)-Si(42)-C(45)	113.23(9)
C(43)-Si(42)-C(45)	110.42(9)
C(46)-C(45)-C(47)	108.65(19)
C(46)-C(45)-C(48)	108.94(18)
C(47)-C(45)-C(48)	108.66(17)
C(46)-C(45)-Si(42)	110.22(14)
C(47)-C(45)-Si(42)	111.78(13)
C(48)-C(45)-Si(42)	108.55(14)
C(5)-C(51)-C(52)	110.16(15)
C(62)-C(61)-C(6)	115.46(16)
C(7)-O(71)-C(72)	114.02(14)
O(111)-C(111)-Mn	178.0(3)
O(112)-C(112)-Mn	176.2(2)
O(113)-C(113)-Mn	176.4(2)
O(121)-C(121)-Cr	178.25(17)
O(122)-C(122)-Cr	177.30(18)
O(123)-C(123)-Cr	178.71(18)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **7**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn	43(1)	27(1)	31(1)	1(1)	-2(1)	4(1)
Cr	23(1)	26(1)	22(1)	2(1)	6(1)	2(1)
C(1)	66(2)	37(1)	35(1)	-9(1)	4(1)	16(1)
C(2)	62(2)	32(1)	31(1)	-6(1)	-9(1)	5(1)
C(3)	39(1)	29(1)	30(1)	-1(1)	-7(1)	4(1)
C(3A)	35(1)	26(1)	24(1)	2(1)	3(1)	7(1)
C(3B)	26(1)	27(1)	22(1)	4(1)	6(1)	5(1)
C(4)	20(1)	26(1)	22(1)	3(1)	5(1)	1(1)
C(5)	24(1)	28(1)	21(1)	3(1)	6(1)	1(1)
C(6)	27(1)	27(1)	23(1)	3(1)	5(1)	-3(1)
C(7)	21(1)	35(1)	24(1)	8(1)	4(1)	-1(1)
C(7A)	25(1)	31(1)	26(1)	7(1)	8(1)	5(1)
C(8)	29(1)	46(1)	35(1)	6(1)	13(1)	9(1)
C(9)	43(1)	48(1)	41(1)	3(1)	19(1)	20(1)
C(9A)	46(1)	35(1)	29(1)	0(1)	9(1)	13(1)
O(41)	21(1)	29(1)	31(1)	2(1)	5(1)	-2(1)
Si(42)	22(1)	28(1)	25(1)	-1(1)	5(1)	-1(1)
C(43)	33(1)	45(1)	30(1)	-6(1)	2(1)	3(1)

C(44)	31(1)	36(1)	37(1)	3(1)	1(1)	1(1)
C(45)	25(1)	36(1)	31(1)	-1(1)	9(1)	-5(1)
C(46)	59(2)	52(1)	77(2)	25(1)	34(1)	3(1)
C(47)	47(1)	69(2)	37(1)	-14(1)	20(1)	-20(1)
C(48)	29(1)	78(2)	41(1)	-4(1)	8(1)	-14(1)
C(51)	27(1)	30(1)	29(1)	-6(1)	10(1)	0(1)
C(52)	40(1)	48(1)	30(1)	-6(1)	14(1)	-8(1)
C(61)	35(1)	35(1)	36(1)	-6(1)	8(1)	-9(1)
C(62)	40(1)	31(1)	51(1)	-1(1)	10(1)	-8(1)
O(71)	20(1)	46(1)	33(1)	11(1)	5(1)	-4(1)
C(72)	26(1)	70(2)	42(1)	19(1)	-1(1)	-6(1)
C(111)	56(2)	52(1)	52(2)	15(1)	-2(1)	7(1)
O(111)	59(1)	101(2)	94(2)	37(1)	-12(1)	19(1)
C(112)	73(2)	39(1)	38(1)	-1(1)	-6(1)	-5(1)
O(112)	124(2)	55(1)	60(1)	9(1)	2(1)	-41(1)
C(113)	50(1)	37(1)	33(1)	4(1)	-5(1)	-5(1)
O(113)	74(1)	65(1)	34(1)	-13(1)	3(1)	1(1)
C(121)	32(1)	35(1)	27(1)	-1(1)	6(1)	0(1)
O(121)	49(1)	35(1)	58(1)	3(1)	3(1)	13(1)
C(122)	32(1)	39(1)	28(1)	5(1)	5(1)	1(1)
O(122)	46(1)	67(1)	44(1)	15(1)	18(1)	-14(1)
C(123)	36(1)	33(1)	29(1)	2(1)	10(1)	0(1)
O(123)	58(1)	62(1)	32(1)	-10(1)	4(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **7**.

	x	y	z	U(eq)
H(1)	6909	4628	1473	56
H(2)	8867	4664	1398	52
H(3)	9408	3483	650	41
H(8)	5037	2349	515	43
H(9)	5321	3505	1066	51
H(43A)	10887	3188	1588	54
H(43B)	11514	2526	2185	54
H(43C)	10251	2595	2137	54
H(44A)	10389	1033	1378	52
H(44B)	11632	1158	1354	52
H(44C)	10870	883	339	52
H(46A)	11140	3548	-209	91
H(46B)	10444	3179	-1195	91
H(46C)	11656	3402	-1230	91
H(47A)	12018	2151	-1741	75
H(47B)	10809	1933	-1683	75
H(47C)	11768	1488	-1037	75
H(48A)	13138	2717	-261	74
H(48B)	12913	2061	468	74
H(48C)	12678	2871	788	74
H(51A)	8851	415	-1127	34
H(51B)	9669	1070	-848	34
H(52A)	8080	1019	-2659	57
H(52B)	9330	911	-2661	57
H(52C)	8883	1680	-2378	57
H(61A)	6092	447	-1825	42

H(61B)	7309	198	-1687	42
H(62A)	7129	-397	-145	60
H(62B)	6236	-683	-1053	60
H(62C)	5926	-118	-226	60
H(72A)	4438	1925	-1254	70
H(72B)	3876	1152	-1275	70
H(72C)	4854	1277	-1891	70

2.2 *Syn*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-6-methoxy-9-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9a]}manganese (8)

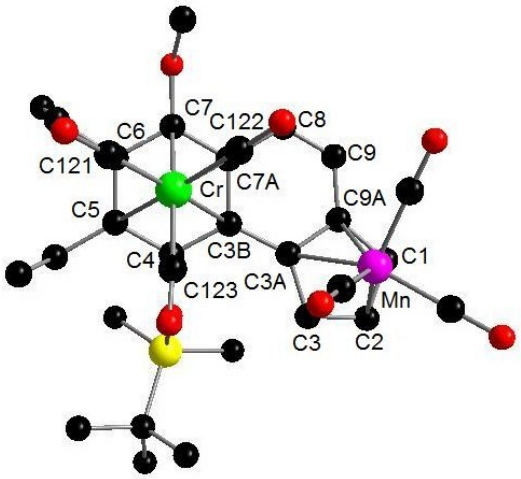


Table 1. Crystal data and structure refinement for **8**.

Empirical formula C_{30} H_{33} Cr Mn O_8 Si

Formula weight 656.59

Temperature 198(2) K

Wavelength 0.71073 Å

Crystal system, space group monoclinic, $P2_1/n$ (No.14)

Unit cell dimensions a = 10.5548(1) Å
b = 14.1276(2) Å β = 94.663(1)°.
c = 20.5362(2) Å

Volume 3052.10(6) Å^3

Z, Calculated density 4, 1.429 Mg/m^3

Absorption coefficient 0.857 mm^{-1}

F(000) 1360

Crystal size 0.45 x 0.35 x 0.15 mm

Theta range for data collection 1.75 to 27.87°.

Limiting indices	-13<=h<=9, -17<=k<=18, -24<=l<=26
Reflections collected / unique	17934 / 7259 [R(int) = 0.0384]
Completeness to theta = 27.87	99.7 %
Max. and min. transmission	0.8823 and 0.6992
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7259 / 0 / 378
Goodness-of-fit on F^2	1.055
Final R indices [I>2σ(I)]	R1 = 0.0366, wR^2 = 0.0862
R indices (all data)	R1 = 0.0528, wR^2 = 0.0925
Largest diff. peak and hole	0.361 and -0.544 eÅ^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **8**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mn	12793(1)	1414(1)	3178(1)	30(1)
Cr	9208(1)	1874(1)	1909(1)	22(1)
C(1)	13936(2)	2652(2)	3135(1)	41(1)
C(2)	14322(2)	1974(2)	2691(1)	41(1)
C(3)	13301(2)	1783(2)	2219(1)	32(1)
C(3A)	12275(2)	2398(1)	2349(1)	26(1)
C(3B)	11070(2)	2639(1)	1983(1)	21(1)
C(4)	10762(2)	2427(1)	1308(1)	20(1)
O(41)	11630(1)	1965(1)	974(1)	23(1)
Si(42)	12698(1)	2436(1)	494(1)	25(1)
C(43)	14090(2)	2927(2)	990(1)	45(1)
C(44)	12023(2)	3424(2)	-15(1)	52(1)
C(45)	13134(2)	1391(1)	2(1)	30(1)
C(46)	13536(2)	562(2)	453(1)	41(1)
C(47)	14254(2)	1662(2)	-399(1)	49(1)
C(48)	12010(2)	1082(2)	-469(1)	44(1)
C(5)	9559(2)	2655(1)	987(1)	21(1)
C(51)	9252(2)	2396(1)	274(1)	28(1)
C(52)	8534(2)	1479(2)	146(1)	47(1)
C(6)	8663(2)	3157(1)	1336(1)	23(1)
C(61)	7378(2)	3444(1)	1022(1)	29(1)
C(62)	7414(2)	4432(2)	724(1)	40(1)
C(7)	9017(2)	3464(1)	1977(1)	26(1)
O(71)	8229(1)	4081(1)	2269(1)	36(1)
C(72)	7403(3)	3685(2)	2718(1)	61(1)
C(7A)	10216(2)	3239(1)	2298(1)	24(1)
C(8)	10623(2)	3679(1)	2922(1)	33(1)

C(9)	11799(2)	3556(1)	3207(1)	38(1)
C(9A)	12658(2)	2914(1)	2932(1)	33(1)
C(111)	13871(2)	667(2)	3655(1)	48(1)
O(111)	14557(2)	188(2)	3964(1)	78(1)
C(112)	11871(2)	391(2)	2938(1)	40(1)
O(112)	11294(2)	-286(1)	2816(1)	61(1)
C(113)	11892(2)	1580(2)	3872(1)	38(1)
O(113)	11340(2)	1686(1)	4324(1)	59(1)
C(121)	7589(2)	1439(1)	1723(1)	34(1)
O(121)	6567(1)	1151(1)	1610(1)	55(1)
C(122)	9054(2)	1478(2)	2755(1)	37(1)
O(122)	8931(2)	1238(1)	3280(1)	63(1)
C(123)	9787(2)	706(1)	1670(1)	29(1)
O(123)	10155(2)	-6(1)	1484(1)	45(1)

Table 3. Bond lengths [Å] and angles [°] for **8**.

Mn-C(111)	1.785(2)
Mn-C(112)	1.789(2)
Mn-C(113)	1.792(2)
Mn-C(2)	2.120(2)
Mn-C(1)	2.130(2)
Mn-C(3)	2.146(2)
Mn-C(9A)	2.181(2)
Mn-C(3A)	2.2322(18)
Cr-C(121)	1.827(2)
Cr-C(123)	1.839(2)
Cr-C(122)	1.845(2)
Cr-C(6)	2.2113(17)
Cr-C(3B)	2.2375(17)
Cr-C(5)	2.2484(17)
Cr-C(7)	2.2615(18)
Cr-C(4)	2.2689(16)
Cr-C(7A)	2.3140(18)
C(1)-C(2)	1.406(3)
C(1)-C(9A)	1.428(3)
C(2)-C(3)	1.415(3)
C(3)-C(3A)	1.431(3)
C(3A)-C(9A)	1.432(3)
C(3A)-C(3B)	1.463(2)
C(3B)-C(4)	1.429(2)
C(3B)-C(7A)	1.431(2)
C(4)-O(41)	1.357(2)
C(4)-C(5)	1.420(2)
O(41)-Si(42)	1.6924(12)
Si(42)-C(44)	1.852(2)
Si(42)-C(43)	1.853(2)
Si(42)-C(45)	1.8686(19)
C(45)-C(46)	1.531(3)
C(45)-C(48)	1.532(3)
C(45)-C(47)	1.542(3)
C(5)-C(6)	1.423(2)
C(5)-C(51)	1.517(2)
C(51)-C(52)	1.513(3)
C(6)-C(7)	1.407(3)
C(6)-C(61)	1.510(2)
C(61)-C(62)	1.526(3)

C(7)-O(71)	1.376(2)
C(7)-C(7A)	1.414(3)
O(71)-C(72)	1.433(3)
C(7A)-C(8)	1.457(3)
C(8)-C(9)	1.340(3)
C(9)-C(9A)	1.430(3)
C(111)-O(111)	1.144(3)
C(112)-O(112)	1.151(3)
C(113)-O(113)	1.145(3)
C(121)-O(121)	1.158(2)
C(122)-O(122)	1.148(3)
C(123)-O(123)	1.154(2)
C(111)-Mn-C(112)	88.96(11)
C(111)-Mn-C(113)	89.83(10)
C(112)-Mn-C(113)	90.69(10)
C(111)-Mn-C(2)	90.21(10)
C(112)-Mn-C(2)	126.16(10)
C(113)-Mn-C(2)	143.14(10)
C(111)-Mn-C(1)	99.78(10)
C(112)-Mn-C(1)	161.67(9)
C(113)-Mn-C(1)	105.31(10)
C(2)-Mn-C(1)	38.64(9)
C(111)-Mn-C(3)	116.81(9)
C(112)-Mn-C(3)	96.59(9)
C(113)-Mn-C(3)	152.39(8)
C(2)-Mn-C(3)	38.74(8)
C(1)-Mn-C(3)	65.09(8)
C(111)-Mn-C(9A)	136.75(10)
C(112)-Mn-C(9A)	134.22(8)
C(113)-Mn-C(9A)	91.62(9)
C(2)-Mn-C(9A)	64.26(8)
C(1)-Mn-C(9A)	38.67(8)
C(3)-Mn-C(9A)	64.41(8)
C(111)-Mn-C(3A)	153.21(9)
C(112)-Mn-C(3A)	101.50(8)
C(113)-Mn-C(3A)	114.35(8)
C(2)-Mn-C(3A)	63.65(7)
C(1)-Mn-C(3A)	64.01(7)
C(3)-Mn-C(3A)	38.09(7)
C(9A)-Mn-C(3A)	37.84(7)
C(121)-Cr-C(123)	88.15(9)
C(121)-Cr-C(122)	86.69(9)
C(123)-Cr-C(122)	92.09(9)
C(121)-Cr-C(6)	88.06(8)
C(123)-Cr-C(6)	132.18(8)
C(122)-Cr-C(6)	135.19(8)
C(121)-Cr-C(3B)	168.04(8)
C(123)-Cr-C(3B)	98.22(7)
C(122)-Cr-C(3B)	103.09(8)
C(6)-Cr-C(3B)	80.15(6)
C(121)-Cr-C(5)	101.79(8)
C(123)-Cr-C(5)	97.75(7)
C(122)-Cr-C(5)	167.16(8)
C(6)-Cr-C(5)	37.19(6)
C(3B)-Cr-C(5)	67.43(6)
C(121)-Cr-C(7)	105.10(8)
C(123)-Cr-C(7)	160.21(7)
C(122)-Cr-C(7)	103.12(8)
C(6)-Cr-C(7)	36.63(7)
C(3B)-Cr-C(7)	66.29(6)

C(5)-Cr-C(7)	65.55(6)
C(121)-Cr-C(4)	135.02(8)
C(123)-Cr-C(4)	83.91(7)
C(122)-Cr-C(4)	137.66(8)
C(6)-Cr-C(4)	66.24(6)
C(3B)-Cr-C(4)	36.96(6)
C(5)-Cr-C(4)	36.63(6)
C(7)-Cr-C(4)	76.32(6)
C(121)-Cr-C(7A)	138.44(8)
C(123)-Cr-C(7A)	133.39(7)
C(122)-Cr-C(7A)	89.99(8)
C(6)-Cr-C(7A)	65.95(6)
C(3B)-Cr-C(7A)	36.60(6)
C(5)-Cr-C(7A)	77.26(6)
C(7)-Cr-C(7A)	35.99(6)
C(4)-Cr-C(7A)	64.46(6)
C(2)-C(1)-C(9A)	107.67(18)
C(2)-C(1)-Mn	70.30(13)
C(9A)-C(1)-Mn	72.61(12)
C(1)-C(2)-C(3)	109.25(19)
C(1)-C(2)-Mn	71.07(13)
C(3)-C(2)-Mn	71.64(12)
C(2)-C(3)-C(3A)	107.60(18)
C(2)-C(3)-Mn	69.61(12)
C(3A)-C(3)-Mn	74.20(11)
C(3)-C(3A)-C(9A)	107.36(16)
C(3)-C(3A)-C(3B)	133.26(17)
C(9A)-C(3A)-C(3B)	119.04(16)
C(3)-C(3A)-Mn	67.71(10)
C(9A)-C(3A)-Mn	69.15(11)
C(3B)-C(3A)-Mn	133.25(13)
C(4)-C(3B)-C(7A)	117.45(15)
C(4)-C(3B)-C(3A)	124.67(15)
C(7A)-C(3B)-C(3A)	117.31(15)
C(4)-C(3B)-Cr	72.71(9)
C(7A)-C(3B)-Cr	74.61(10)
C(3A)-C(3B)-Cr	130.12(12)
O(41)-C(4)-C(5)	119.28(15)
O(41)-C(4)-C(3B)	118.80(15)
C(5)-C(4)-C(3B)	121.88(15)
O(41)-C(4)-Cr	131.10(11)
C(5)-C(4)-Cr	70.90(9)
C(3B)-C(4)-Cr	70.32(9)
C(4)-O(41)-Si(42)	127.94(11)
O(41)-Si(42)-C(44)	112.43(9)
O(41)-Si(42)-C(43)	111.28(9)
C(44)-Si(42)-C(43)	106.24(12)
O(41)-Si(42)-C(45)	102.05(7)
C(44)-Si(42)-C(45)	113.00(11)
C(43)-Si(42)-C(45)	111.98(10)
C(46)-C(45)-C(48)	109.02(17)
C(46)-C(45)-C(47)	109.04(17)
C(48)-C(45)-C(47)	108.77(17)
C(46)-C(45)-Si(42)	110.22(13)
C(48)-C(45)-Si(42)	110.76(14)
C(47)-C(45)-Si(42)	108.99(15)
C(4)-C(5)-C(6)	118.94(15)
C(4)-C(5)-C(51)	120.43(15)
C(6)-C(5)-C(51)	120.59(15)
C(4)-C(5)-Cr	72.47(10)

C(6)-C(5)-Cr	69.99(9)
C(51)-C(5)-Cr	131.04(12)
C(52)-C(51)-C(5)	116.02(16)
C(7)-C(6)-C(5)	119.30(16)
C(7)-C(6)-C(61)	118.61(16)
C(5)-C(6)-C(61)	121.89(16)
C(7)-C(6)-Cr	73.62(10)
C(5)-C(6)-Cr	72.82(10)
C(61)-C(6)-Cr	129.30(12)
C(6)-C(61)-C(62)	111.49(16)
O(71)-C(7)-C(6)	118.64(16)
O(71)-C(7)-C(7A)	119.22(16)
C(6)-C(7)-C(7A)	121.78(16)
O(71)-C(7)-Cr	135.75(13)
C(6)-C(7)-Cr	69.74(10)
C(7A)-C(7)-Cr	74.03(10)
C(7)-O(71)-C(72)	117.04(16)
C(7)-C(7A)-C(3B)	119.64(16)
C(7)-C(7A)-C(8)	120.21(16)
C(3B)-C(7A)-C(8)	119.95(16)
C(7)-C(7A)-Cr	69.98(10)
C(3B)-C(7A)-Cr	68.79(10)
C(8)-C(7A)-Cr	138.98(13)
C(9)-C(8)-C(7A)	121.62(18)
C(8)-C(9)-C(9A)	120.34(18)
C(1)-C(9A)-C(9)	131.51(19)
C(1)-C(9A)-C(3A)	107.97(18)
C(9)-C(9A)-C(3A)	120.52(18)
C(1)-C(9A)-Mn	68.72(12)
C(9)-C(9A)-Mn	123.78(15)
C(3A)-C(9A)-Mn	73.01(11)
O(111)-C(111)-Mn	179.5(2)
O(112)-C(112)-Mn	176.47(19)
O(113)-C(113)-Mn	178.5(2)
O(121)-C(121)-Cr	179.01(19)
O(122)-C(122)-Cr	178.5(2)
O(123)-C(123)-Cr	175.99(17)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **8**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn	31(1)	31(1)	26(1)	1(1)	-4(1)	7(1)
Cr	21(1)	23(1)	24(1)	3(1)	4(1)	-1(1)
C(1)	36(1)	43(1)	40(1)	4(1)	-15(1)	-6(1)
C(2)	25(1)	55(1)	41(1)	10(1)	-4(1)	2(1)
C(3)	28(1)	40(1)	28(1)	3(1)	1(1)	5(1)
C(3A)	25(1)	27(1)	25(1)	1(1)	0(1)	-1(1)
C(3B)	21(1)	22(1)	21(1)	0(1)	1(1)	-2(1)
C(4)	19(1)	20(1)	22(1)	0(1)	4(1)	-3(1)
O(41)	20(1)	26(1)	24(1)	-1(1)	6(1)	1(1)
Si(42)	22(1)	23(1)	30(1)	2(1)	7(1)	-2(1)
C(43)	35(1)	50(1)	52(1)	-4(1)	7(1)	-18(1)

C(44)	45(1)	36(1)	78(2)	28(1)	17(1)	4(1)
C(45)	31(1)	32(1)	28(1)	1(1)	12(1)	0(1)
C(46)	47(1)	30(1)	46(1)	2(1)	10(1)	9(1)
C(47)	42(1)	60(2)	47(1)	6(1)	26(1)	3(1)
C(48)	47(1)	48(1)	35(1)	-12(1)	4(1)	-2(1)
C(5)	20(1)	22(1)	23(1)	2(1)	2(1)	-4(1)
C(51)	26(1)	36(1)	23(1)	2(1)	-1(1)	-2(1)
C(52)	61(2)	45(1)	32(1)	-6(1)	-5(1)	-16(1)
C(6)	20(1)	22(1)	28(1)	6(1)	3(1)	-2(1)
C(61)	21(1)	30(1)	36(1)	5(1)	0(1)	1(1)
C(62)	36(1)	32(1)	51(1)	10(1)	-6(1)	5(1)
C(7)	27(1)	23(1)	28(1)	1(1)	8(1)	4(1)
O(71)	37(1)	36(1)	38(1)	-3(1)	11(1)	15(1)
C(72)	62(2)	69(2)	56(2)	1(1)	35(1)	19(1)
C(7A)	30(1)	21(1)	23(1)	1(1)	3(1)	0(1)
C(8)	48(1)	27(1)	25(1)	-6(1)	1(1)	7(1)
C(9)	54(1)	28(1)	28(1)	-6(1)	-10(1)	1(1)
C(9A)	37(1)	29(1)	30(1)	1(1)	-7(1)	-3(1)
C(111)	42(1)	50(1)	49(1)	8(1)	-2(1)	12(1)
O(111)	59(1)	80(1)	92(2)	35(1)	-13(1)	29(1)
C(112)	55(1)	32(1)	31(1)	3(1)	-3(1)	7(1)
O(112)	90(1)	33(1)	57(1)	2(1)	-11(1)	-10(1)
C(113)	43(1)	39(1)	30(1)	2(1)	-5(1)	10(1)
O(113)	67(1)	75(1)	36(1)	1(1)	11(1)	19(1)
C(121)	28(1)	34(1)	41(1)	11(1)	5(1)	0(1)
O(121)	27(1)	57(1)	79(1)	12(1)	0(1)	-11(1)
C(122)	39(1)	37(1)	34(1)	4(1)	5(1)	-7(1)
O(122)	80(1)	77(1)	33(1)	18(1)	14(1)	-14(1)
C(123)	27(1)	28(1)	32(1)	5(1)	1(1)	-4(1)
O(123)	54(1)	30(1)	51(1)	-5(1)	-1(1)	8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **8**.

	x	y	z	U(eq)
H(1)	14435	2891	3505	49
H(2)	15140	1690	2705	49
H(3)	13298	1328	1878	38
H(43A)	13797	3324	1340	68
H(43B)	14599	3311	711	68
H(43C)	14610	2408	1182	68
H(44A)	11434	3172	-366	78
H(44B)	12712	3766	-205	78
H(44C)	11567	3857	256	78
H(46A)	12833	393	715	61
H(46B)	14277	746	743	61
H(46C)	13753	16	189	61
H(47A)	14998	1817	-101	73
H(47B)	14018	2212	-673	73
H(47C)	14457	1128	-677	73
H(48A)	12266	546	-731	65
H(48B)	11745	1610	-758	65
H(48C)	11300	891	-219	65
H(51A)	8746	2916	60	34

H(51B)	10060	2357	62	34
H(52A)	9031	952	346	70
H(52B)	8393	1375	-326	70
H(52C)	7713	1515	336	70
H(61A)	6748	3432	1353	35
H(61B)	7103	2982	676	35
H(62A)	7665	4893	1067	60
H(62B)	6569	4594	521	60
H(62C)	8030	4443	392	60
H(72A)	6853	3207	2493	91
H(72B)	6877	4187	2885	91
H(72C)	7913	3388	3083	91
H(8)	10040	4063	3133	40
H(9)	12064	3896	3593	45

2.3 *Anti*-tricarbonyl-{tricarbonyl(ŋ^6-5a,6,7,8,9,9a-(7,8-diethyl-9-methoxy-6-[(*tert*-butyl)dimethylsilyloxy]benzo[*e*]indenyl)chromium[ŋ^5-1,2,3,3a,9a]}manganese (9)

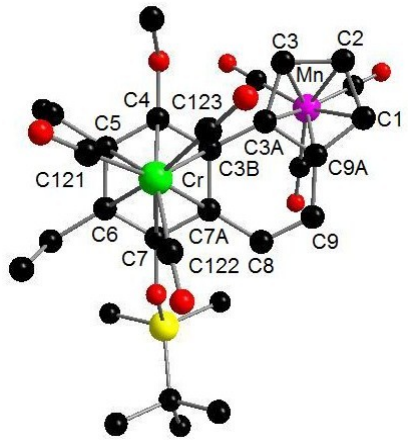


Table 1. Crystal data and structure refinement for **9**.

Empirical formula	C_{30} H_{33} Cr Mn O_8 Si
Formula weight	656.59
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c (No.15)
Unit cell dimensions	a = 24.6752(3) Å b = 9.9320(1) Å β = 92.790(1)°. c = 24.9507(3) Å
Volume	6107.52(12) Å^3
Z, Calculated density	8, 1.428 Mg/m^3
Absorption coefficient	0.856 mm^{-1}
F(000)	2720

Crystal size	0.60 x 0.30 x 0.20 mm
Theta range for data collection	2.21 to 28.29°.
Limiting indices	-31<=h<=32, -12<=k<=13, -32<=l<=32
Reflections collected / unique	23072 / 7462 [R(int) = 0.042]
Completeness to theta = 28.29	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8474 and 0.6276
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7462 / 0 / 378
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R1 = 0.0362, wR^2 = 0.0921
R indices (all data)	R1 = 0.0516, wR^2 = 0.0997
Largest diff. peak and hole	0.602 and -0.368 eÅ^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **9**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mn	5579(1)	10068(1)	1494(1)	25(1)
Cr	4002(1)	6758(1)	679(1)	23(1)
C(1)	5600(1)	10346(2)	641(1)	32(1)
C(2)	5949(1)	9277(2)	806(1)	34(1)
C(3)	5642(1)	8259(2)	1041(1)	29(1)
C(3A)	5084(1)	8673(2)	1016(1)	23(1)
C(3B)	4586(1)	8033(2)	1175(1)	20(1)
C(4)	4563(1)	6736(2)	1413(1)	22(1)
O(41)	5043(1)	6083(1)	1549(1)	29(1)
C(42)	5224(1)	5086(2)	1178(1)	38(1)
C(5)	4066(1)	6148(2)	1541(1)	25(1)
C(51)	4066(1)	4786(2)	1811(1)	34(1)
C(52)	4111(1)	4917(2)	2419(1)	48(1)
C(6)	3572(1)	6886(2)	1456(1)	25(1)
C(61)	3028(1)	6315(2)	1604(1)	38(1)
C(62)	2688(1)	5709(3)	1150(1)	63(1)
C(7)	3597(1)	8200(2)	1249(1)	23(1)
O(71)	3135(1)	8938(1)	1178(1)	27(1)
Si(72)	2894(1)	10125(1)	1583(1)	27(1)
C(73)	2683(1)	9375(3)	2222(1)	52(1)
C(74)	3423(1)	11400(3)	1759(1)	50(1)

C(75)	2310(1)	10857(2)	1179(1)	45(1)
C(76)	2501(1)	11365(4)	640(1)	84(1)
C(77)	2083(1)	12039(3)	1502(2)	75(1)
C(78)	1860(1)	9810(3)	1085(1)	68(1)
C(7A)	4092(1)	8773(2)	1077(1)	20(1)
C(8)	4094(1)	10054(2)	798(1)	24(1)
C(9)	4552(1)	10650(2)	652(1)	26(1)
C(9A)	5063(1)	9969(2)	761(1)	25(1)
C(111)	5653(1)	9151(2)	2114(1)	39(1)
O(111)	5709(1)	8575(2)	2507(1)	70(1)
C(112)	6142(1)	11132(3)	1676(1)	46(1)
O(112)	6505(1)	11814(2)	1795(1)	76(1)
C(113)	5113(1)	11232(2)	1769(1)	38(1)
O(113)	4805(1)	11969(2)	1934(1)	67(1)
C(121)	3837(1)	4998(2)	508(1)	36(1)
O(121)	3751(1)	3877(2)	407(1)	58(1)
C(122)	3508(1)	7392(2)	159(1)	39(1)
O(122)	3209(1)	7846(2)	-157(1)	69(1)
C(123)	4521(1)	6654(2)	179(1)	30(1)
O(123)	4851(1)	6602(2)	-132(1)	47(1)

Table 3. Bond lengths [Å] and angles [°] for **9**.

Mn-C(112)	1.785(2)
Mn-C(113)	1.791(2)
Mn-C(111)	1.797(2)
Mn-C(2)	2.133(2)
Mn-C(3)	2.133(2)
Mn-C(1)	2.1488(19)
Mn-C(3A)	2.1651(18)
Mn-C(9A)	2.1803(18)
Cr-C(123)	1.832(2)
Cr-C(121)	1.840(2)
Cr-C(122)	1.846(2)
Cr-C(5)	2.2324(18)
Cr-C(7A)	2.2403(17)
Cr-C(4)	2.2417(17)
Cr-C(3B)	2.2446(17)
Cr-C(6)	2.2584(18)
Cr-C(7)	2.2833(17)
C(1)-C(2)	1.417(3)
C(1)-C(9A)	1.422(3)
C(2)-C(3)	1.408(3)
C(3)-C(3A)	1.434(2)
C(3A)-C(9A)	1.436(2)
C(3A)-C(3B)	1.457(2)
C(3B)-C(4)	1.421(2)
C(3B)-C(7A)	1.433(2)
C(4)-O(41)	1.379(2)
C(4)-C(5)	1.408(3)
O(41)-C(42)	1.440(2)
C(5)-C(6)	1.429(3)
C(5)-C(51)	1.512(2)
C(51)-C(52)	1.523(3)
C(6)-C(7)	1.405(3)
C(6)-C(61)	1.519(3)
C(61)-C(62)	1.503(3)

C(7)-O(71)	1.360(2)
C(7)-C(7A)	1.433(2)
O(71)-Si(72)	1.6795(14)
Si(72)-C(74)	1.856(2)
Si(72)-C(73)	1.858(2)
Si(72)-C(75)	1.864(2)
C(75)-C(78)	1.531(4)
C(75)-C(76)	1.533(4)
C(75)-C(77)	1.545(4)
C(7A)-C(8)	1.451(2)
C(8)-C(9)	1.343(3)
C(9)-C(9A)	1.444(3)
C(111)-O(111)	1.137(3)
C(112)-O(112)	1.152(3)
C(113)-O(113)	1.145(3)
C(121)-O(121)	1.160(2)
C(122)-O(122)	1.146(3)
C(123)-O(123)	1.153(2)
C(112)-Mn-C(113)	91.52(11)
C(112)-Mn-C(111)	92.09(11)
C(113)-Mn-C(111)	92.12(10)
C(112)-Mn-C(2)	93.67(10)
C(113)-Mn-C(2)	148.69(9)
C(111)-Mn-C(2)	118.48(10)
C(112)-Mn-C(3)	123.90(10)
C(113)-Mn-C(3)	144.25(9)
C(111)-Mn-C(3)	91.32(9)
C(2)-Mn-C(3)	38.56(8)
C(112)-Mn-C(1)	96.90(10)
C(113)-Mn-C(1)	110.06(9)
C(111)-Mn-C(1)	155.72(10)
C(2)-Mn-C(1)	38.65(8)
C(3)-Mn-C(1)	64.98(8)
C(112)-Mn-C(3A)	158.28(9)
C(113)-Mn-C(3A)	105.57(8)
C(111)-Mn-C(3A)	100.40(8)
C(2)-Mn-C(3A)	64.77(7)
C(3)-Mn-C(3A)	38.98(7)
C(1)-Mn-C(3A)	64.96(7)
C(112)-Mn-C(9A)	130.94(9)
C(113)-Mn-C(9A)	89.46(8)
C(111)-Mn-C(9A)	136.90(9)
C(2)-Mn-C(9A)	64.17(7)
C(3)-Mn-C(9A)	64.63(7)
C(1)-Mn-C(9A)	38.35(7)
C(3A)-Mn-C(9A)	38.59(6)
C(123)-Cr-C(121)	86.77(9)
C(123)-Cr-C(122)	90.00(10)
C(121)-Cr-C(122)	91.74(10)
C(123)-Cr-C(5)	128.44(8)
C(121)-Cr-C(5)	88.25(8)
C(122)-Cr-C(5)	141.46(9)
C(123)-Cr-C(7A)	107.11(8)
C(121)-Cr-C(7A)	165.27(8)
C(122)-Cr-C(7A)	93.11(8)
C(5)-Cr-C(7A)	79.31(6)
C(123)-Cr-C(4)	97.62(8)
C(121)-Cr-C(4)	107.51(8)
C(122)-Cr-C(4)	159.58(8)
C(5)-Cr-C(4)	36.68(7)

C(7A)-Cr-C(4)	66.56(6)
C(123)-Cr-C(3B)	87.55(7)
C(121)-Cr-C(3B)	142.44(8)
C(122)-Cr-C(3B)	125.36(8)
C(5)-Cr-C(3B)	66.92(6)
C(7A)-Cr-C(3B)	37.26(6)
C(4)-Cr-C(3B)	36.92(6)
C(123)-Cr-C(6)	163.77(8)
C(121)-Cr-C(6)	98.27(8)
C(122)-Cr-C(6)	105.18(9)
C(5)-Cr-C(6)	37.11(7)
C(7A)-Cr-C(6)	67.03(6)
C(4)-Cr-C(6)	66.15(7)
C(3B)-Cr-C(6)	79.03(6)
C(123)-Cr-C(7)	143.20(8)
C(121)-Cr-C(7)	129.85(8)
C(122)-Cr-C(7)	85.94(8)
C(5)-Cr-C(7)	65.32(7)
C(7A)-Cr-C(7)	36.93(6)
C(4)-Cr-C(7)	76.60(6)
C(3B)-Cr-C(7)	65.85(6)
C(6)-Cr-C(7)	36.04(6)
C(2)-C(1)-C(9A)	107.61(17)
C(2)-C(1)-Mn	70.06(11)
C(9A)-C(1)-Mn	72.02(11)
C(3)-C(2)-C(1)	108.99(17)
C(3)-C(2)-Mn	70.73(11)
C(1)-C(2)-Mn	71.30(11)
C(2)-C(3)-C(3A)	108.16(17)
C(2)-C(3)-Mn	70.71(12)
C(3A)-C(3)-Mn	71.73(11)
C(3)-C(3A)-C(9A)	106.91(16)
C(3)-C(3A)-C(3B)	133.18(17)
C(9A)-C(3A)-C(3B)	119.87(16)
C(3)-C(3A)-Mn	69.30(10)
C(9A)-C(3A)-Mn	71.28(10)
C(3B)-C(3A)-Mn	126.19(12)
C(4)-C(3B)-C(7A)	119.07(15)
C(4)-C(3B)-C(3A)	124.10(16)
C(7A)-C(3B)-C(3A)	116.82(15)
C(4)-C(3B)-Cr	71.43(9)
C(7A)-C(3B)-Cr	71.21(9)
C(3A)-C(3B)-Cr	128.56(12)
O(41)-C(4)-C(5)	119.82(16)
O(41)-C(4)-C(3B)	118.52(15)
C(5)-C(4)-C(3B)	121.56(16)
O(41)-C(4)-Cr	133.90(12)
C(5)-C(4)-Cr	71.30(10)
C(3B)-C(4)-Cr	71.65(9)
C(4)-O(41)-C(42)	117.09(14)
C(4)-C(5)-C(6)	119.93(16)
C(4)-C(5)-C(51)	119.37(17)
C(6)-C(5)-C(51)	120.49(17)
C(4)-C(5)-Cr	72.02(10)
C(6)-C(5)-Cr	72.43(10)
C(51)-C(5)-Cr	132.12(13)
C(5)-C(51)-C(52)	111.50(17)
C(7)-C(6)-C(5)	118.63(16)
C(7)-C(6)-C(61)	119.39(17)
C(5)-C(6)-C(61)	121.93(17)

C(7)-C(6)-Cr	72.94(10)
C(5)-C(6)-Cr	70.46(10)
C(61)-C(6)-Cr	130.18(14)
C(62)-C(61)-C(6)	115.75(19)
O(71)-C(7)-C(6)	119.82(16)
O(71)-C(7)-C(7A)	117.97(15)
C(6)-C(7)-C(7A)	122.10(16)
O(71)-C(7)-Cr	130.33(12)
C(6)-C(7)-Cr	71.01(10)
C(7A)-C(7)-Cr	69.91(9)
C(7)-O(71)-Si(72)	128.24(11)
O(71)-Si(72)-C(74)	110.87(9)
O(71)-Si(72)-C(73)	110.93(10)
C(74)-Si(72)-C(73)	107.00(13)
O(71)-Si(72)-C(75)	103.63(9)
C(74)-Si(72)-C(75)	112.17(12)
C(73)-Si(72)-C(75)	112.30(12)
C(78)-C(75)-C(76)	109.9(3)
C(78)-C(75)-C(77)	108.5(2)
C(76)-C(75)-C(77)	110.0(3)
C(78)-C(75)-Si(72)	110.69(18)
C(76)-C(75)-Si(72)	109.95(17)
C(77)-C(75)-Si(72)	107.79(18)
C(3B)-C(7A)-C(7)	118.35(15)
C(3B)-C(7A)-C(8)	120.71(16)
C(7)-C(7A)-C(8)	120.93(15)
C(3B)-C(7A)-Cr	71.53(9)
C(7)-C(7A)-Cr	73.16(10)
C(8)-C(7A)-Cr	125.01(12)
C(9)-C(8)-C(7A)	122.54(17)
C(8)-C(9)-C(9A)	118.80(17)
C(1)-C(9A)-C(3A)	108.30(16)
C(1)-C(9A)-C(9)	130.56(17)
C(3A)-C(9A)-C(9)	121.12(16)
C(1)-C(9A)-Mn	69.63(11)
C(3A)-C(9A)-Mn	70.13(10)
C(9)-C(9A)-Mn	127.28(13)
O(111)-C(111)-Mn	178.8(2)
O(112)-C(112)-Mn	179.7(3)
O(113)-C(113)-Mn	178.2(2)
O(121)-C(121)-Cr	177.6(2)
O(122)-C(122)-Cr	176.7(2)
O(123)-C(123)-Cr	179.11(19)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **9**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn	22(1)	25(1)	27(1)	5(1)	0(1)	-3(1)
Cr	26(1)	22(1)	21(1)	-4(1)	1(1)	0(1)
C(1)	27(1)	40(1)	29(1)	9(1)	7(1)	-5(1)
C(2)	23(1)	45(1)	35(1)	2(1)	10(1)	0(1)
C(3)	24(1)	31(1)	33(1)	0(1)	5(1)	4(1)

C(3A)	23(1)	24(1)	22(1)	0(1)	2(1)	1(1)
C(3B)	23(1)	21(1)	17(1)	-3(1)	2(1)	0(1)
C(4)	28(1)	19(1)	19(1)	-3(1)	0(1)	3(1)
O(41)	32(1)	24(1)	30(1)	0(1)	-2(1)	8(1)
C(42)	41(1)	30(1)	44(1)	-4(1)	6(1)	13(1)
C(5)	37(1)	19(1)	21(1)	-2(1)	4(1)	-2(1)
C(51)	47(1)	22(1)	35(1)	4(1)	6(1)	-4(1)
C(52)	65(2)	44(1)	33(1)	13(1)	2(1)	-8(1)
C(6)	27(1)	25(1)	26(1)	-4(1)	8(1)	-5(1)
C(61)	34(1)	29(1)	51(1)	2(1)	15(1)	-8(1)
C(62)	34(1)	81(2)	75(2)	-7(2)	2(1)	-24(1)
C(7)	22(1)	24(1)	22(1)	-5(1)	3(1)	0(1)
O(71)	20(1)	29(1)	32(1)	-4(1)	4(1)	1(1)
Si(72)	23(1)	26(1)	33(1)	-2(1)	6(1)	2(1)
C(73)	71(2)	46(1)	40(1)	0(1)	21(1)	8(1)
C(74)	42(1)	47(1)	60(2)	-24(1)	12(1)	-11(1)
C(75)	34(1)	45(1)	56(1)	6(1)	1(1)	12(1)
C(76)	72(2)	112(3)	66(2)	41(2)	-5(2)	25(2)
C(77)	57(2)	56(2)	113(3)	-1(2)	5(2)	30(2)
C(78)	34(1)	80(2)	90(2)	-7(2)	-15(1)	3(1)
C(7A)	22(1)	19(1)	19(1)	-2(1)	1(1)	1(1)
C(8)	25(1)	23(1)	23(1)	3(1)	1(1)	4(1)
C(9)	27(1)	26(1)	24(1)	8(1)	2(1)	0(1)
C(9A)	24(1)	29(1)	21(1)	3(1)	3(1)	-2(1)
C(111)	49(1)	33(1)	35(1)	3(1)	-7(1)	-3(1)
O(111)	109(2)	57(1)	41(1)	21(1)	-14(1)	-3(1)
C(112)	41(1)	49(1)	47(1)	0(1)	4(1)	-15(1)
O(112)	57(1)	87(2)	83(2)	-12(1)	5(1)	-45(1)
C(113)	42(1)	39(1)	33(1)	-2(1)	-8(1)	6(1)
O(113)	69(1)	74(1)	55(1)	-23(1)	-11(1)	36(1)
C(121)	39(1)	35(1)	34(1)	-8(1)	3(1)	-3(1)
O(121)	69(1)	33(1)	71(1)	-20(1)	3(1)	-12(1)
C(122)	41(1)	42(1)	34(1)	-9(1)	-5(1)	4(1)
O(122)	69(1)	83(1)	52(1)	-4(1)	-30(1)	22(1)
C(123)	42(1)	24(1)	25(1)	-2(1)	5(1)	0(1)
O(123)	65(1)	39(1)	39(1)	-2(1)	27(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **9**.

	x	y	z	U(eq)
H(1)	5704	11165	480	38
H(2)	6330	9251	766	41
H(3)	5780	7440	1189	35
H(42A)	4920	4495	1069	57
H(42B)	5515	4549	1352	57
H(42C)	5358	5534	861	57
H(51A)	4375	4248	1690	41
H(51B)	3727	4303	1703	41
H(52A)	4449	5383	2527	71
H(52B)	4111	4018	2582	71
H(52C)	3802	5433	2541	71
H(61A)	3095	5615	1882	45
H(61B)	2817	7044	1766	45

H(62A)	2632	6376	863	95
H(62B)	2336	5434	1280	95
H(62C)	2874	4920	1010	95
H(73A)	2373	8775	2150	77
H(73B)	2580	10094	2466	77
H(73C)	2986	8860	2388	77
H(74A)	3754	10946	1896	74
H(74B)	3292	12004	2035	74
H(74C)	3501	11923	1439	74
H(76A)	2613	10599	424	126
H(76B)	2808	11981	702	126
H(76C)	2202	11842	448	126
H(77A)	1780	12456	1295	113
H(77B)	2369	12709	1573	113
H(77C)	1955	11702	1843	113
H(78A)	1559	10210	869	103
H(78B)	1730	9516	1431	103
H(78C)	2003	9034	894	103
H(8)	3757	10489	715	28
H(9)	4541	11504	480	31

2.4 Tricarbonyl-{pentacarbonyl[8-benzo[*e*]indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,9a]}manganese (16)

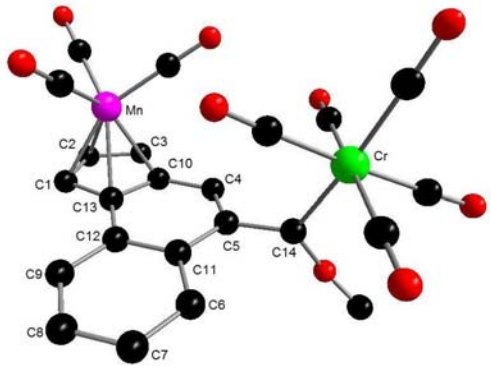


Table 1. Crystal data and structure refinement for **16**.

Empirical formula	C_{23} H_{11} Cr Mn O_9
Formula weight	538.26
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P1bar (No. 2)
Unit cell dimensions	a = 6.760(1) Å α = 85.86(1)°. b = 7.520(1) Å β = 83.38(1)°. c = 21.444(1) Å γ = 88.90(1)°.
Volume	1080.0(2) Å^3

Z, Calculated density	2, 1.655 Mg/m^3
Absorption coefficient	1.142 mm^{-1}
F(000)	540
Crystal size	0.35 x 0.20 x 0.10 mm
Theta range for data collection	0.96 to 28.54°.
Limiting indices	0<=h<=8, -9<=k<=9, -28<=l<=28
Reflections collected / unique	10176 / 5235 [R(int) = 0.052]
Completeness to theta = 28.54	95.5 %
Max. and min. transmission	0.8944 and 0.6908
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3272 / 3 / 316
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R1 = 0.0662, wR^2 = 0.1287
R indices (all data)	R1 = 0.1195, wR^2 = 0.1552
Largest diff. peak and hole	0.797 and -0.649 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **16**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mn(1)	834(1)	-57(1)	1151(1)	39(1)
Cr(1)	-2701(1)	-589(1)	3779(1)	56(1)
C(1)	1178(7)	-2674(6)	819(2)	49(1)
C(2)	3048(7)	-1921(6)	833(2)	51(1)
C(3)	3298(6)	-1564(6)	1449(2)	47(1)
C(4)	1027(6)	-2206(6)	2503(2)	45(1)
C(5)	-726(6)	-2915(6)	2763(2)	41(1)
C(6)	-3809(7)	-4583(6)	2659(2)	49(1)
C(7)	-4987(7)	-5418(6)	2299(3)	56(1)
C(8)	-4497(8)	-5430(6)	1654(3)	59(1)
C(9)	-2819(7)	-4574(6)	1373(2)	49(1)
C(10)	1558(6)	-2189(6)	1839(2)	41(1)
C(11)	-2061(6)	-3724(5)	2385(2)	41(1)
C(12)	-1590(6)	-3709(5)	1727(2)	41(1)
C(13)	250(6)	-2873(6)	1450(2)	42(1)
C(14)	-1341(6)	-2774(7)	3453(2)	52(1)
O(15A)	-780(20)	-4389(9)	3676(4)	73(2)
C(16A)	-949(16)	-4862(13)	4343(4)	69(2)

O(15B)	-770(30)	-3946(13)	3894(4)	73(2)
C(16B)	380(20)	-5454(14)	3677(6)	69(2)
C(17)	-5079(8)	-1864(8)	4034(3)	64(1)
O(18)	-6482(6)	-2637(6)	4184(2)	93(1)
C(19)	-2031(7)	-1051(7)	4600(3)	59(1)
O(20)	-1669(7)	-1275(6)	5108(2)	87(1)
C(21)	-3927(9)	1559(9)	4012(3)	75(2)
O(22)	-4676(8)	2884(7)	4147(2)	109(2)
C(23)	-204(8)	554(9)	3565(2)	70(2)
O(24)	1335(6)	1177(7)	3454(2)	92(2)
C(25)	-3518(7)	-18(7)	2969(3)	54(1)
O(26)	-4076(6)	357(5)	2499(2)	72(1)
C(27)	-1556(7)	422(6)	898(2)	45(1)
O(28)	-3082(5)	756(5)	733(2)	65(1)
C(29)	515(7)	1486(6)	1749(2)	48(1)
O(30)	373(6)	2473(5)	2135(2)	71(1)
C(31)	1928(7)	1632(7)	613(2)	51(1)
O(32)	2634(6)	2749(5)	263(2)	73(1)

Table 3. Bond lengths [Å] and angles [°] for **16**.

Mn(1)-C(31)	1.766(5)
Mn(1)-C(29)	1.782(5)
Mn(1)-C(27)	1.785(5)
Mn(1)-C(2)	2.120(4)
Mn(1)-C(3)	2.130(4)
Mn(1)-C(1)	2.141(4)
Mn(1)-C(10)	2.186(4)
Mn(1)-C(13)	2.198(4)
Cr(1)-C(21)	1.875(7)
Cr(1)-C(19)	1.875(6)
Cr(1)-C(17)	1.893(6)
Cr(1)-C(25)	1.900(6)
Cr(1)-C(23)	1.902(5)
Cr(1)-C(14)	1.998(5)
C(1)-C(2)	1.399(7)
C(1)-C(13)	1.423(6)
C(2)-C(3)	1.396(6)
C(3)-C(10)	1.429(6)
C(4)-C(5)	1.353(6)
C(4)-C(10)	1.427(6)
C(5)-C(11)	1.450(6)
C(5)-C(14)	1.501(6)
C(6)-C(7)	1.362(7)
C(6)-C(11)	1.404(6)
C(7)-C(8)	1.385(7)
C(8)-C(9)	1.371(7)
C(9)-C(12)	1.389(6)
C(10)-C(13)	1.410(6)
C(11)-C(12)	1.410(6)
C(12)-C(13)	1.450(6)
C(14)-O(15B)	1.331(7)
C(14)-O(15A)	1.337(7)
O(15A)-C(16A)	1.442(10)
O(15B)-C(16B)	1.438(11)
C(17)-O(18)	1.125(6)
C(19)-O(20)	1.144(6)

C(21)-O(22)	1.149(7)
C(23)-O(24)	1.142(6)
C(25)-O(26)	1.132(6)
C(27)-O(28)	1.146(5)
C(29)-O(30)	1.146(5)
C(31)-O(32)	1.157(5)
C(31)-Mn(1)-C(29)	89.9(2)
C(31)-Mn(1)-C(27)	91.1(2)
C(29)-Mn(1)-C(27)	93.7(2)
C(31)-Mn(1)-C(2)	91.1(2)
C(29)-Mn(1)-C(2)	136.4(2)
C(27)-Mn(1)-C(2)	129.9(2)
C(31)-Mn(1)-C(3)	104.36(19)
C(29)-Mn(1)-C(3)	99.7(2)
C(27)-Mn(1)-C(3)	159.5(2)
C(2)-Mn(1)-C(3)	38.37(17)
C(31)-Mn(1)-C(1)	113.7(2)
C(29)-Mn(1)-C(1)	153.8(2)
C(27)-Mn(1)-C(1)	96.9(2)
C(2)-Mn(1)-C(1)	38.34(18)
C(3)-Mn(1)-C(1)	64.76(18)
C(31)-Mn(1)-C(10)	142.34(19)
C(29)-Mn(1)-C(10)	90.74(19)
C(27)-Mn(1)-C(10)	126.45(18)
C(2)-Mn(1)-C(10)	63.60(17)
C(3)-Mn(1)-C(10)	38.64(16)
C(1)-Mn(1)-C(10)	63.78(17)
C(31)-Mn(1)-C(13)	151.7(2)
C(29)-Mn(1)-C(13)	116.84(19)
C(27)-Mn(1)-C(13)	95.92(18)
C(2)-Mn(1)-C(13)	63.59(17)
C(3)-Mn(1)-C(13)	64.19(17)
C(1)-Mn(1)-C(13)	38.28(16)
C(10)-Mn(1)-C(13)	37.52(16)
C(21)-Cr(1)-C(19)	89.8(3)
C(21)-Cr(1)-C(17)	91.5(2)
C(19)-Cr(1)-C(17)	87.8(2)
C(21)-Cr(1)-C(25)	86.7(2)
C(19)-Cr(1)-C(25)	176.2(2)
C(17)-Cr(1)-C(25)	90.9(2)
C(21)-Cr(1)-C(23)	91.3(3)
C(19)-Cr(1)-C(23)	88.5(2)
C(17)-Cr(1)-C(23)	175.3(3)
C(25)-Cr(1)-C(23)	93.0(2)
C(21)-Cr(1)-C(14)	174.9(2)
C(19)-Cr(1)-C(14)	94.7(2)
C(17)-Cr(1)-C(14)	91.2(2)
C(25)-Cr(1)-C(14)	88.9(2)
C(23)-Cr(1)-C(14)	86.3(2)
C(2)-C(1)-C(13)	107.5(4)
C(2)-C(1)-Mn(1)	70.0(3)
C(13)-C(1)-Mn(1)	73.0(3)
C(3)-C(2)-C(1)	109.8(4)
C(3)-C(2)-Mn(1)	71.2(3)
C(1)-C(2)-Mn(1)	71.6(3)
C(2)-C(3)-C(10)	106.9(4)
C(2)-C(3)-Mn(1)	70.4(2)
C(10)-C(3)-Mn(1)	72.8(2)
C(5)-C(4)-C(10)	119.7(4)
C(4)-C(5)-C(11)	121.5(4)

C(4)-C(5)-C(14)	118.9(4)
C(11)-C(5)-C(14)	119.5(4)
C(7)-C(6)-C(11)	120.8(5)
C(6)-C(7)-C(8)	120.8(5)
C(9)-C(8)-C(7)	119.7(5)
C(8)-C(9)-C(12)	120.8(5)
C(13)-C(10)-C(4)	120.5(4)
C(13)-C(10)-C(3)	108.2(4)
C(4)-C(10)-C(3)	131.3(4)
C(13)-C(10)-Mn(1)	71.7(2)
C(4)-C(10)-Mn(1)	125.4(3)
C(3)-C(10)-Mn(1)	68.5(2)
C(6)-C(11)-C(12)	118.2(4)
C(6)-C(11)-C(5)	121.7(4)
C(12)-C(11)-C(5)	120.1(4)
C(9)-C(12)-C(11)	119.7(4)
C(9)-C(12)-C(13)	122.3(4)
C(11)-C(12)-C(13)	117.9(4)
C(10)-C(13)-C(1)	107.6(4)
C(10)-C(13)-C(12)	120.2(4)
C(1)-C(13)-C(12)	132.1(4)
C(10)-C(13)-Mn(1)	70.8(2)
C(1)-C(13)-Mn(1)	68.7(3)
C(12)-C(13)-Mn(1)	129.3(3)
O(15B)-C(14)-O(15A)	25.8(6)
O(15B)-C(14)-C(5)	122.9(6)
O(15A)-C(14)-C(5)	99.9(5)
O(15B)-C(14)-Cr(1)	114.8(5)
O(15A)-C(14)-Cr(1)	138.5(5)
C(5)-C(14)-Cr(1)	121.5(3)
C(14)-O(15A)-C(16A)	120.9(7)
C(14)-O(15B)-C(16B)	116.5(8)
O(18)-C(17)-Cr(1)	179.3(6)
O(20)-C(19)-Cr(1)	177.2(5)
O(22)-C(21)-Cr(1)	179.1(6)
O(24)-C(23)-Cr(1)	176.7(6)
O(26)-C(25)-Cr(1)	177.0(4)
O(28)-C(27)-Mn(1)	178.9(4)
O(30)-C(29)-Mn(1)	177.8(4)
O(32)-C(31)-Mn(1)	179.4(5)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **16**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn(1)	33(1)	49(1)	36(1)	-2(1)	-2(1)	1(1)
Cr(1)	46(1)	81(1)	40(1)	-16(1)	5(1)	-20(1)
C(1)	57(3)	50(3)	42(3)	-10(2)	-7(2)	9(2)
C(2)	43(3)	63(3)	43(3)	-4(2)	5(2)	15(2)
C(3)	31(2)	67(3)	43(3)	-2(2)	-4(2)	7(2)
C(4)	36(2)	64(3)	35(2)	-4(2)	-8(2)	3(2)
C(5)	39(2)	45(2)	40(2)	1(2)	-5(2)	5(2)
C(6)	47(3)	42(2)	56(3)	1(2)	-1(2)	1(2)

C(7)	49(3)	41(3)	77(4)	-2(2)	-6(3)	-6(2)
C(8)	61(3)	45(3)	74(4)	-13(2)	-18(3)	-4(2)
C(9)	55(3)	45(3)	50(3)	-4(2)	-9(2)	1(2)
C(10)	36(2)	46(2)	40(2)	-2(2)	-2(2)	11(2)
C(11)	39(2)	35(2)	49(3)	1(2)	-6(2)	3(2)
C(12)	44(2)	33(2)	45(3)	-2(2)	-9(2)	7(2)
C(13)	42(2)	48(3)	36(2)	-3(2)	-4(2)	10(2)
C(14)	33(2)	82(4)	40(3)	3(2)	-5(2)	-12(2)
O(15A)	70(3)	129(5)	17(5)	32(4)	-19(5)	-23(4)
C(16A)	82(6)	75(5)	51(5)	4(4)	-13(4)	2(4)
O(15B)	70(3)	129(5)	17(5)	32(4)	-19(5)	-23(4)
C(16B)	82(6)	75(5)	51(5)	4(4)	-13(4)	2(4)
C(17)	51(3)	74(4)	67(4)	-15(3)	4(3)	-8(3)
O(18)	54(2)	96(3)	124(4)	-13(3)	16(2)	-29(2)
C(19)	52(3)	72(3)	53(3)	-14(3)	7(2)	-20(2)
O(20)	102(3)	114(3)	45(2)	-3(2)	-9(2)	-28(3)
C(21)	77(4)	79(4)	64(4)	-17(3)	19(3)	-30(3)
O(22)	134(4)	78(3)	104(4)	-24(3)	43(3)	-23(3)
C(23)	62(3)	114(5)	35(3)	-13(3)	-2(2)	-31(3)
O(24)	64(3)	154(4)	58(3)	-5(3)	0(2)	-55(3)
C(25)	44(3)	57(3)	61(3)	-19(3)	-1(2)	-3(2)
O(26)	82(3)	67(2)	71(3)	-11(2)	-30(2)	13(2)
C(27)	40(3)	50(3)	45(3)	-2(2)	-1(2)	-4(2)
O(28)	36(2)	91(3)	68(2)	-1(2)	-8(2)	3(2)
C(29)	49(3)	49(3)	46(3)	-1(2)	-7(2)	0(2)
O(30)	92(3)	62(2)	61(2)	-19(2)	-18(2)	12(2)
C(31)	41(3)	65(3)	46(3)	-2(2)	-2(2)	1(2)
O(32)	67(2)	81(3)	65(3)	18(2)	3(2)	-16(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **16**.

	x	y	z	U(eq)
H(1)	634	-2991	459	59
H(2)	3994	-1690	481	61
H(3)	4400	-1017	1582	57
H(4)	1892	-1725	2759	53
H(6)	-4170	-4581	3095	59
H(7)	-6147	-5994	2491	67
H(8)	-5312	-6022	1411	71
H(9)	-2496	-4574	934	59
H(16A)	-34	-4153	4536	104
H(16B)	-627	-6117	4416	104
H(16C)	-2301	-4634	4527	104
H(16D)	-120	-5844	3304	104
H(16E)	279	-6419	4004	104
H(16F)	1767	-5117	3575	104

2.5 *Anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (17)

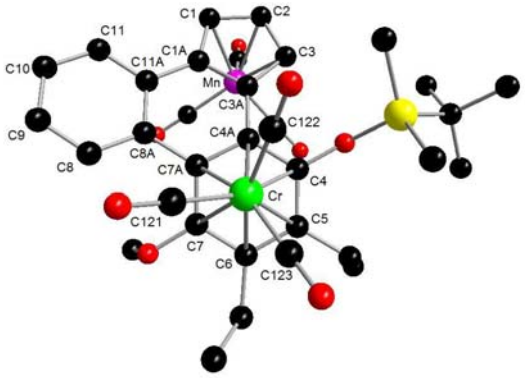


Table 1. Crystal data and structure refinement for **FRO3987**.

Empirical formula	$C_{35}\ H_{37}\ Cl_2\ Cr\ Mn\ O_8\ Si$
Formula weight	791.58
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$ (No.14)
Unit cell dimensions	a = 14.3645(2) Å b = 14.1696(2) Å β = 111.194(1)°. c = 19.2953(4) Å
Volume	3661.71(11) $Å^3$
Z, Calculated density	4, 1.436 Mg/m^3
Absorption coefficient	0.869 mm^{-1}
F(000)	1632
Crystal size	0.15 x 0.15 x 0.10 mm
Theta range for data collection	1.83 to 26.30°.
Limiting indices	-17<=h<=17, -16<=k<=17, -24<=l<=20
Reflections collected / unique	24362 / 7414 [R(int) = 0.0683]
Completeness to theta = 26.30	99.9 %
Max. and min. transmission	0.9182 and 0.8807
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7414 / 0 / 441
Goodness-of-fit on F^2	1.019
Final R indices [I>2σ(I)]	R1 = 0.0491, wR^2 = 0.1060

R indices (all data) R1 = 0.0932, wR^2 = 0.1212

Largest diff. peak and hole 0.689 and -0.674 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **17**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mn	2172(1)	6691(1)	2972(1)	32(1)
Cr	3339(1)	3058(1)	2850(1)	27(1)
C(1A)	3479(2)	5950(2)	3697(2)	30(1)
C(1)	3701(3)	6924(2)	3676(2)	37(1)
C(2)	3564(3)	7152(2)	2936(2)	43(1)
C(3)	3237(3)	6345(2)	2482(2)	35(1)
C(3A)	3192(2)	5579(2)	2960(2)	28(1)
C(4A)	2804(2)	4616(2)	2800(2)	25(1)
C(4)	2472(2)	4212(2)	2072(2)	26(1)
C(5)	1907(2)	3373(2)	1910(2)	29(1)
C(6)	1664(2)	2923(2)	2481(2)	31(1)
C(7)	2038(2)	3294(2)	3207(2)	29(1)
C(7A)	2674(2)	4104(2)	3399(2)	25(1)
C(8A)	3165(2)	4433(2)	4178(2)	28(1)
C(8)	3327(3)	3832(2)	4792(2)	36(1)
C(9)	3820(3)	4142(2)	5506(2)	43(1)
C(10)	4148(3)	5064(3)	5638(2)	44(1)
C(11)	4012(3)	5667(2)	5054(2)	38(1)
C(11A)	3537(2)	5355(2)	4324(2)	29(1)
O(41)	2623(2)	4705(1)	1511(1)	28(1)
Si(42)	3449(1)	4680(1)	1075(1)	31(1)
C(43)	4604(3)	5315(3)	1633(2)	47(1)
C(44)	3794(3)	3459(2)	912(2)	42(1)
C(45)	2785(3)	5303(2)	166(2)	39(1)
C(46)	2501(3)	6310(3)	304(2)	61(1)
C(47)	3488(3)	5340(3)	-272(2)	57(1)
C(48)	1831(3)	4775(3)	-293(2)	57(1)
C(51)	1456(3)	3034(2)	1117(2)	38(1)
C(52)	398(3)	3433(3)	743(2)	56(1)
C(61)	970(3)	2072(2)	2336(2)	43(1)
C(62)	1443(3)	1149(2)	2693(2)	57(1)
O(71)	1757(2)	2844(1)	3730(1)	40(1)
C(72)	992(3)	3346(3)	3902(2)	58(1)
C(111)	1181(3)	6357(2)	2131(2)	47(1)
O(111)	575(2)	6133(2)	1584(2)	75(1)
C(112)	1514(3)	6332(3)	3558(2)	50(1)
O(112)	1122(2)	6082(2)	3948(2)	85(1)
C(113)	1709(3)	7870(2)	2924(2)	50(1)
O(113)	1415(3)	8628(2)	2902(2)	85(1)
C(121)	4002(3)	2448(2)	3725(2)	40(1)
O(121)	4442(2)	2070(2)	4281(1)	60(1)
C(122)	4574(3)	3363(2)	2859(2)	36(1)
O(122)	5385(2)	3512(2)	2888(2)	56(1)
C(123)	3424(3)	1980(2)	2355(2)	35(1)
O(123)	3479(2)	1301(2)	2037(1)	53(1)

C(100)	1989(5)	9465(4)	1043(5)	139(3)
Cl(1)	1033(2)	10226(1)	809(1)	129(1)
Cl(2)	1735(2)	8326(1)	1038(1)	129(1)

Table 3. Bond lengths [Å] and angles [°] for **17**.

Mn-C(113)	1.787(4)
Mn-C(112)	1.791(4)
Mn-C(111)	1.792(4)
Mn-C(3)	2.125(3)
Mn-C(2)	2.127(3)
Mn-C(1)	2.149(3)
Mn-C(3A)	2.157(3)
Mn-C(1A)	2.164(3)
Cr-C(122)	1.820(4)
Cr-C(123)	1.828(3)
Cr-C(121)	1.829(3)
Cr-C(7A)	2.229(3)
Cr-C(7)	2.238(3)
Cr-C(5)	2.240(3)
Cr-C(6)	2.258(3)
Cr-C(4)	2.264(3)
Cr-C(4A)	2.329(3)
C(1A)-C(1)	1.421(4)
C(1A)-C(3A)	1.430(4)
C(1A)-C(11A)	1.452(4)
C(1)-C(2)	1.405(5)
C(2)-C(3)	1.414(4)
C(3)-C(3A)	1.440(4)
C(3A)-C(4A)	1.464(4)
C(4A)-C(4)	1.430(4)
C(4A)-C(7A)	1.432(4)
C(4)-O(41)	1.370(3)
C(4)-C(5)	1.409(4)
C(5)-C(6)	1.421(4)
C(5)-C(51)	1.509(4)
C(6)-C(7)	1.408(4)
C(6)-C(61)	1.523(4)
C(7)-O(71)	1.373(4)
C(7)-C(7A)	1.430(4)
C(7A)-C(8A)	1.486(4)
C(8A)-C(11A)	1.401(4)
C(8A)-C(8)	1.409(4)
C(8)-C(9)	1.374(5)
C(9)-C(10)	1.382(5)
C(10)-C(11)	1.372(5)
C(11)-C(11A)	1.396(4)
O(41)-Si(42)	1.684(2)
Si(42)-C(43)	1.852(4)
Si(42)-C(44)	1.858(3)
Si(42)-C(45)	1.886(3)
C(45)-C(48)	1.530(5)
C(45)-C(47)	1.534(5)
C(45)-C(46)	1.535(5)
C(51)-C(52)	1.536(5)
C(61)-C(62)	1.519(5)
O(71)-C(72)	1.445(4)

C(111)-O(111)	1.144(4)
C(112)-O(112)	1.147(4)
C(113)-O(113)	1.150(4)
C(121)-O(121)	1.161(4)
C(122)-O(122)	1.165(4)
C(123)-O(123)	1.159(4)
C(100)-Cl(2)	1.654(5)
C(100)-Cl(1)	1.674(6)
C(113)-Mn-C(112)	91.50(17)
C(113)-Mn-C(111)	92.33(16)
C(112)-Mn-C(111)	93.90(18)
C(113)-Mn-C(3)	120.47(16)
C(112)-Mn-C(3)	147.62(14)
C(111)-Mn-C(3)	90.03(15)
C(113)-Mn-C(2)	92.79(16)
C(112)-Mn-C(2)	145.55(16)
C(111)-Mn-C(2)	120.03(16)
C(3)-Mn-C(2)	38.84(12)
C(113)-Mn-C(1)	99.53(15)
C(112)-Mn-C(1)	107.26(16)
C(111)-Mn-C(1)	155.31(15)
C(3)-Mn-C(1)	65.28(13)
C(2)-Mn-C(1)	38.37(13)
C(113)-Mn-C(3A)	157.44(16)
C(112)-Mn-C(3A)	108.36(13)
C(111)-Mn-C(3A)	96.76(14)
C(3)-Mn-C(3A)	39.29(11)
C(2)-Mn-C(3A)	64.79(12)
C(1)-Mn-C(3A)	64.96(12)
C(113)-Mn-C(1A)	134.96(14)
C(112)-Mn-C(1A)	89.24(14)
C(111)-Mn-C(1A)	132.55(13)
C(3)-Mn-C(1A)	65.17(12)
C(2)-Mn-C(1A)	64.16(13)
C(1)-Mn-C(1A)	38.46(11)
C(3A)-Mn-C(1A)	38.65(11)
C(122)-Cr-C(123)	87.41(15)
C(122)-Cr-C(121)	85.56(16)
C(123)-Cr-C(121)	88.69(14)
C(122)-Cr-C(7A)	114.90(12)
C(123)-Cr-C(7A)	157.69(14)
C(121)-Cr-C(7A)	92.55(12)
C(122)-Cr-C(7)	151.74(12)
C(123)-Cr-C(7)	120.43(13)
C(121)-Cr-C(7)	90.02(14)
C(7A)-Cr-C(7)	37.34(10)
C(122)-Cr-C(5)	124.57(13)
C(123)-Cr-C(5)	87.65(13)
C(121)-Cr-C(5)	149.40(15)
C(7A)-Cr-C(5)	79.99(11)
C(7)-Cr-C(5)	66.09(11)
C(122)-Cr-C(6)	161.38(13)
C(123)-Cr-C(6)	91.68(13)
C(121)-Cr-C(6)	113.02(14)
C(7A)-Cr-C(6)	67.36(11)
C(7)-Cr-C(6)	36.51(11)
C(5)-Cr-C(6)	36.83(11)
C(122)-Cr-C(4)	97.81(13)
C(123)-Cr-C(4)	112.45(12)
C(121)-Cr-C(4)	158.66(12)

C(7A)-Cr-C(4)	66.84(10)
C(7)-Cr-C(4)	77.02(11)
C(5)-Cr-C(4)	36.47(10)
C(6)-Cr-C(4)	65.42(11)
C(122)-Cr-C(4A)	94.67(12)
C(123)-Cr-C(4A)	148.64(12)
C(121)-Cr-C(4A)	122.67(12)
C(7A)-Cr-C(4A)	36.55(10)
C(7)-Cr-C(4A)	64.58(10)
C(5)-Cr-C(4A)	65.47(10)
C(6)-Cr-C(4A)	76.64(10)
C(4)-Cr-C(4A)	36.23(10)
C(1)-C(1A)-C(3A)	108.4(3)
C(1)-C(1A)-C(11A)	129.9(3)
C(3A)-C(1A)-C(11A)	121.6(3)
C(1)-C(1A)-Mn	70.18(18)
C(3A)-C(1A)-Mn	70.42(17)
C(11A)-C(1A)-Mn	126.5(2)
C(2)-C(1)-C(1A)	107.5(3)
C(2)-C(1)-Mn	70.0(2)
C(1A)-C(1)-Mn	71.37(18)
C(1)-C(2)-C(3)	109.7(3)
C(1)-C(2)-Mn	71.6(2)
C(3)-C(2)-Mn	70.52(19)
C(2)-C(3)-C(3A)	107.1(3)
C(2)-C(3)-Mn	70.6(2)
C(3A)-C(3)-Mn	71.55(18)
C(1A)-C(3A)-C(3)	107.2(2)
C(1A)-C(3A)-C(4A)	120.1(3)
C(3)-C(3A)-C(4A)	132.1(3)
C(1A)-C(3A)-Mn	70.93(17)
C(3)-C(3A)-Mn	69.15(17)
C(4A)-C(3A)-Mn	118.3(2)
C(4)-C(4A)-C(7A)	119.7(3)
C(4)-C(4A)-C(3A)	123.1(3)
C(7A)-C(4A)-C(3A)	117.0(3)
C(4)-C(4A)-Cr	69.41(15)
C(7A)-C(4A)-Cr	67.91(15)
C(3A)-C(4A)-Cr	141.3(2)
O(41)-C(4)-C(5)	119.8(3)
O(41)-C(4)-C(4A)	118.7(2)
C(5)-C(4)-C(4A)	121.1(3)
O(41)-C(4)-Cr	133.2(2)
C(5)-C(4)-Cr	70.85(16)
C(4A)-C(4)-Cr	74.36(16)
C(4)-C(5)-C(6)	119.4(3)
C(4)-C(5)-C(51)	119.7(3)
C(6)-C(5)-C(51)	120.5(3)
C(4)-C(5)-Cr	72.68(17)
C(6)-C(5)-Cr	72.25(18)
C(51)-C(5)-Cr	133.5(2)
C(7)-C(6)-C(5)	119.3(3)
C(7)-C(6)-C(61)	117.8(3)
C(5)-C(6)-C(61)	122.8(3)
C(7)-C(6)-Cr	70.99(18)
C(5)-C(6)-Cr	70.92(18)
C(61)-C(6)-Cr	132.6(2)
O(71)-C(7)-C(6)	116.7(3)
O(71)-C(7)-C(7A)	120.8(3)
C(6)-C(7)-C(7A)	122.5(3)

O(71)-C(7)-Cr	131.1(2)
C(6)-C(7)-Cr	72.50(18)
C(7A)-C(7)-Cr	70.97(17)
C(7)-C(7A)-C(4A)	117.0(3)
C(7)-C(7A)-C(8A)	122.7(3)
C(4A)-C(7A)-C(8A)	120.3(3)
C(7)-C(7A)-Cr	71.69(16)
C(4A)-C(7A)-Cr	75.53(16)
C(8A)-C(7A)-Cr	124.2(2)
C(11A)-C(8A)-C(8)	117.5(3)
C(11A)-C(8A)-C(7A)	120.1(3)
C(8)-C(8A)-C(7A)	122.3(3)
C(9)-C(8)-C(8A)	121.2(3)
C(8)-C(9)-C(10)	120.4(3)
C(11)-C(10)-C(9)	120.0(3)
C(10)-C(11)-C(11A)	120.3(3)
C(11)-C(11A)-C(8A)	120.6(3)
C(11)-C(11A)-C(1A)	121.1(3)
C(8A)-C(11A)-C(1A)	118.1(3)
C(4)-O(41)-Si(42)	136.53(19)
O(41)-Si(42)-C(43)	110.12(14)
O(41)-Si(42)-C(44)	112.56(13)
C(43)-Si(42)-C(44)	108.26(17)
O(41)-Si(42)-C(45)	104.14(14)
C(43)-Si(42)-C(45)	111.04(16)
C(44)-Si(42)-C(45)	110.72(15)
C(48)-C(45)-C(47)	109.2(3)
C(48)-C(45)-C(46)	108.4(3)
C(47)-C(45)-C(46)	109.5(3)
C(48)-C(45)-Si(42)	110.8(2)
C(47)-C(45)-Si(42)	108.5(2)
C(46)-C(45)-Si(42)	110.5(2)
C(5)-C(51)-C(52)	110.4(3)
C(62)-C(61)-C(6)	116.3(3)
C(7)-O(71)-C(72)	113.0(3)
O(111)-C(111)-Mn	177.4(4)
O(112)-C(112)-Mn	177.4(3)
O(113)-C(113)-Mn	179.2(3)
O(121)-C(121)-Cr	178.6(4)
O(122)-C(122)-Cr	176.1(3)
O(123)-C(123)-Cr	179.5(3)
Cl(2)-C(100)-Cl(1)	118.0(4)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **17**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn	36(1)	24(1)	36(1)	0(1)	14(1)	2(1)
Cr	30(1)	26(1)	25(1)	-1(1)	10(1)	4(1)
C(1A)	21(2)	31(2)	36(2)	-6(1)	8(2)	-3(1)
C(1)	36(2)	32(2)	43(2)	-9(1)	14(2)	-9(1)
C(2)	50(2)	29(2)	54(2)	-2(2)	25(2)	-14(2)
C(3)	43(2)	32(2)	38(2)	-1(1)	23(2)	-4(1)

C(3A)	26(2)	27(2)	31(2)	-3(1)	12(2)	-4(1)
C(4A)	22(2)	26(2)	27(2)	-1(1)	10(1)	2(1)
C(4)	22(2)	29(2)	28(2)	2(1)	10(1)	6(1)
C(5)	26(2)	28(2)	30(2)	-2(1)	7(1)	0(1)
C(6)	26(2)	27(2)	37(2)	-2(1)	8(2)	-3(1)
C(7)	29(2)	26(2)	35(2)	1(1)	16(2)	0(1)
C(7A)	24(2)	24(2)	29(2)	-3(1)	13(1)	3(1)
C(8A)	26(2)	32(2)	28(2)	-2(1)	13(2)	5(1)
C(8)	43(2)	36(2)	32(2)	0(1)	17(2)	4(2)
C(9)	46(2)	55(2)	30(2)	3(2)	17(2)	8(2)
C(10)	42(2)	63(2)	25(2)	-9(2)	9(2)	4(2)
C(11)	32(2)	45(2)	33(2)	-12(2)	8(2)	0(2)
C(11A)	23(2)	33(2)	31(2)	-3(1)	9(2)	4(1)
O(41)	32(1)	31(1)	24(1)	3(1)	12(1)	1(1)
Si(42)	33(1)	35(1)	27(1)	0(1)	13(1)	1(1)
C(43)	37(2)	58(2)	47(2)	-3(2)	17(2)	-9(2)
C(44)	44(2)	45(2)	41(2)	0(2)	20(2)	8(2)
C(45)	48(2)	43(2)	28(2)	5(1)	15(2)	5(2)
C(46)	79(3)	51(2)	49(2)	11(2)	19(2)	19(2)
C(47)	69(3)	72(3)	38(2)	14(2)	29(2)	7(2)
C(48)	55(3)	74(3)	34(2)	11(2)	7(2)	1(2)
C(51)	38(2)	40(2)	33(2)	-7(1)	8(2)	-7(2)
C(52)	37(2)	75(3)	43(2)	1(2)	-1(2)	-5(2)
C(61)	47(2)	37(2)	46(2)	-7(2)	18(2)	-16(2)
C(62)	78(3)	35(2)	60(3)	0(2)	29(2)	-14(2)
O(71)	54(2)	34(1)	43(1)	0(1)	31(1)	-10(1)
C(72)	52(3)	70(3)	67(3)	-9(2)	40(2)	-17(2)
C(111)	47(3)	42(2)	52(3)	-9(2)	18(2)	6(2)
O(111)	50(2)	93(2)	65(2)	-30(2)	2(2)	3(2)
C(112)	39(2)	61(2)	54(3)	22(2)	20(2)	23(2)
O(112)	59(2)	126(3)	85(2)	53(2)	45(2)	36(2)
C(113)	57(3)	39(2)	46(2)	-2(2)	10(2)	7(2)
O(113)	104(3)	34(2)	100(3)	-6(1)	17(2)	26(2)
C(121)	52(2)	38(2)	31(2)	-2(2)	17(2)	13(2)
O(121)	82(2)	64(2)	33(2)	13(1)	18(2)	37(2)
C(122)	36(2)	39(2)	32(2)	-5(1)	12(2)	8(2)
O(122)	32(2)	79(2)	63(2)	-21(1)	24(1)	0(1)
C(123)	39(2)	36(2)	29(2)	2(1)	10(2)	6(2)
O(123)	78(2)	37(1)	44(2)	-9(1)	21(1)	13(1)
C(100)	93(5)	68(4)	280(9)	-16(5)	95(6)	-8(3)
Cl(1)	143(2)	75(1)	120(1)	-22(1)	-12(1)	22(1)
Cl(2)	167(2)	59(1)	162(2)	9(1)	60(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **17**.

	x	y	z	U(eq)
H(1)	3904	7345	4087	44
H(2)	3675	7756	2768	51
H(3)	3077	6314	1960	42
H(8)	3090	3200	4711	43
H(9)	3936	3720	5911	51
H(10)	4469	5281	6134	53
H(11)	4241	6300	5146	45

H(43A)	4469	5994	1618	71
H(43B)	5125	5193	1429	71
H(43C)	4830	5095	2149	71
H(44A)	4057	3121	1386	63
H(44B)	4306	3482	687	63
H(44C)	3203	3131	576	63
H(46A)	3103	6654	607	92
H(46B)	2032	6286	567	92
H(46C)	2187	6634	-172	92
H(47A)	3156	5669	-744	85
H(47B)	3657	4696	-371	85
H(47C)	4099	5678	19	85
H(48A)	1526	5082	-778	85
H(48B)	1361	4787	-30	85
H(48C)	1995	4120	-364	85
H(51A)	1431	2336	1108	46
H(51B)	1880	3239	838	46
H(52A)	-28	3206	1006	84
H(52B)	123	3223	224	84
H(52C)	424	4124	760	84
H(61A)	422	2225	2514	52
H(61B)	668	1974	1793	52
H(62A)	1945	954	2488	85
H(62B)	927	662	2591	85
H(62C)	1762	1237	3232	85
H(72A)	1249	3962	4117	87
H(72B)	799	2980	4260	87
H(72C)	408	3436	3446	87
H(10A)	2352	9566	700	167
H(10B)	2452	9631	1548	167

2.6 *Syn*-tricarbonyl-{tricarbonyl(η^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[η^5-1,2,3,3a,11b]}manganese (18)

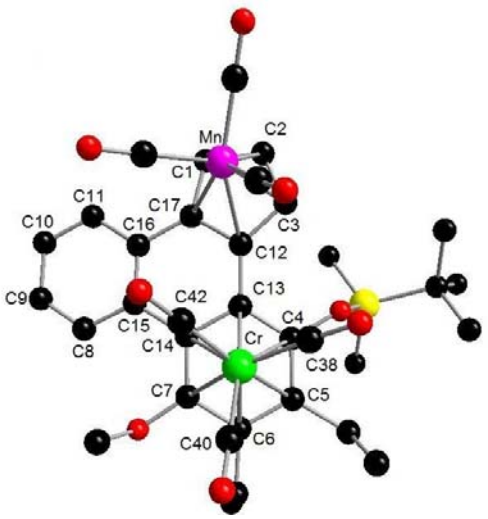


Table 1. Crystal data and structure refinement for **18**.

Empirical formula	C_{35} H_{37} Cl_2 Cr Mn O_8 Si
Formula weight	791.58

Temperature 223(2) K

Wavelength 0.71073 Å

Crystal system, space group monoclinic, $P2_1/n$ (No. 14)

Unit cell dimensions a = 11.512(1) Å $\alpha = 90°$.
b = 15.137(1) Å $\beta = 96.81(1)°$.
c = 21.125(1) Å $\gamma = 90°$.

Volume 3655.2(4) $Å^3$

Z, Calculated density 4, 1.438 Mg/m^3

Absorption coefficient 0.870 mm^{-1}

F(000) 1632

Crystal size 0.45 x 0.30 x 0.10 mm

Theta range for data collection 1.66 to 27.86°.

Limiting indices -15<=h<=14, -18<=k<=19, -27<=l<=24

Reflections collected / unique 22824 / 8620 [R(int) = 0.0752]

Completeness to theta = 27.86 99.2 %

Max. and min. transmission 0.9180 and 0.6955

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 5546 / 1 / 441

Goodness-of-fit on F^2 1.033

Final R indices [I>2σ(I)] R1 = 0.0582, wR^2 = 0.1351

R indices (all data) R1 = 0.1057, wR^2 = 0.1550

Largest diff. peak and hole 1.178 and -0.965 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **18**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr(1)	7455(1)	2873(1)	469(1)	26(1)
Mn(1)	6929(1)	3596(1)	2465(1)	30(1)
C(1)	7984(3)	4726(2)	2719(2)	35(1)
C(2)	8580(3)	3956(2)	2944(2)	35(1)

C(3)	8763(3)	3423(2)	2422(1)	30(1)
C(4)	9272(3)	3100(2)	988(1)	25(1)
C(5)	9359(3)	2905(2)	343(1)	28(1)
C(6)	8718(3)	3439(2)	-126(1)	27(1)
C(7)	8016(3)	4138(2)	60(1)	26(1)
C(8)	6869(3)	5808(2)	498(2)	33(1)
C(9)	6383(3)	6565(2)	709(2)	39(1)
C(10)	6309(3)	6688(2)	1349(2)	43(1)
C(11)	6771(3)	6067(2)	1775(2)	39(1)
C(12)	8340(3)	3885(2)	1852(1)	25(1)
C(13)	8477(3)	3740(2)	1178(1)	24(1)
C(14)	7902(2)	4327(2)	707(1)	25(1)
C(15)	7307(3)	5136(2)	918(1)	26(1)
C(16)	7280(3)	5299(2)	1571(2)	30(1)
C(17)	7821(3)	4674(2)	2038(2)	29(1)
O(18)	9958(2)	2643(2)	1448(1)	29(1)
Si(19)	11359(1)	2903(1)	1718(1)	35(1)
C(20)	11417(4)	3847(3)	2278(2)	64(1)
C(21)	12173(3)	3259(3)	1062(2)	56(1)
C(22)	11932(3)	1855(3)	2111(2)	50(1)
C(23)	13228(4)	1999(5)	2350(3)	95(2)
C(24)	11780(5)	1088(3)	1640(2)	84(2)
C(25)	11280(4)	1636(4)	2676(2)	66(1)
C(26)	10144(3)	2172(2)	154(2)	39(1)
C(27)	9534(4)	1324(3)	-100(2)	62(1)
C(28)	8879(3)	3355(2)	-823(1)	34(1)
C(29)	9822(4)	3987(3)	-986(2)	55(1)
O(30)	7502(2)	4659(2)	-430(1)	32(1)
C(31)	6292(3)	4482(3)	-647(2)	45(1)
C(32)	6447(4)	3318(3)	3207(2)	51(1)
O(33)	6126(3)	3137(3)	3681(2)	86(1)
C(34)	6448(3)	2531(3)	2176(2)	37(1)
O(35)	6119(3)	1845(2)	2018(1)	56(1)
C(36)	5528(3)	4068(3)	2213(2)	43(1)
O(37)	4631(2)	4382(2)	2065(2)	65(1)
C(38)	7521(3)	1797(3)	862(2)	39(1)
O(39)	7608(3)	1112(2)	1099(2)	68(1)
C(40)	6743(3)	2344(2)	-253(2)	39(1)
O(41)	6289(3)	2019(2)	-708(1)	64(1)
C(42)	5991(3)	3077(2)	694(2)	36(1)
O(43)	5064(2)	3215(2)	822(1)	58(1)
C	6519(6)	9849(4)	-325(3)	170(5)
Cl(1)	6958(2)	8956(2)	142(1)	141(1)
Cl(2)	5424(2)	9574(2)	-902(1)	187(1)

Table 3. Bond lengths [Å] and angles [°] for **18**.

Cr(1)-C(38)	1.825(4)
Cr(1)-C(40)	1.829(4)
Cr(1)-C(42)	1.831(4)
Cr(1)-C(6)	2.205(3)
Cr(1)-C(13)	2.221(3)
Cr(1)-C(7)	2.228(3)
Cr(1)-C(5)	2.239(3)
Cr(1)-C(4)	2.270(3)
Cr(1)-C(14)	2.303(3)
Mn(1)-C(32)	1.776(4)

Mn(1)-C(36)	1.786(4)
Mn(1)-C(34)	1.789(4)
Mn(1)-C(2)	2.116(3)
Mn(1)-C(1)	2.129(3)
Mn(1)-C(3)	2.140(3)
Mn(1)-C(17)	2.179(3)
Mn(1)-C(12)	2.236(3)
C(1)-C(2)	1.407(5)
C(1)-C(17)	1.431(4)
C(2)-C(3)	1.403(5)
C(3)-C(12)	1.427(4)
C(4)-O(18)	1.365(4)
C(4)-C(5)	1.411(4)
C(4)-C(13)	1.421(4)
C(5)-C(6)	1.416(4)
C(5)-C(26)	1.514(5)
C(6)-C(7)	1.415(4)
C(6)-C(28)	1.512(4)
C(7)-O(30)	1.377(4)
C(7)-C(14)	1.419(4)
C(8)-C(9)	1.372(5)
C(8)-C(15)	1.405(4)
C(9)-C(10)	1.378(5)
C(10)-C(11)	1.365(5)
C(11)-C(16)	1.393(5)
C(12)-C(17)	1.412(4)
C(12)-C(13)	1.468(4)
C(13)-C(14)	1.435(4)
C(14)-C(15)	1.497(4)
C(15)-C(16)	1.405(4)
C(16)-C(17)	1.453(5)
O(18)-Si(19)	1.693(2)
Si(19)-C(21)	1.844(4)
Si(19)-C(20)	1.850(5)
Si(19)-C(22)	1.874(4)
C(22)-C(25)	1.519(6)
C(22)-C(24)	1.526(7)
C(22)-C(23)	1.533(6)
C(26)-C(27)	1.530(6)
C(28)-C(29)	1.517(5)
O(30)-C(31)	1.439(4)
C(32)-O(33)	1.141(5)
C(34)-O(35)	1.141(4)
C(36)-O(37)	1.146(4)
C(38)-O(39)	1.150(4)
C(40)-O(41)	1.149(4)
C(42)-O(43)	1.151(4)
C-Cl(2)	1.698(5)
C-Cl(1)	1.714(5)
C(38)-Cr(1)-C(40)	88.88(16)
C(38)-Cr(1)-C(42)	91.26(16)
C(40)-Cr(1)-C(42)	87.43(16)
C(38)-Cr(1)-C(6)	127.72(14)
C(40)-Cr(1)-C(6)	87.43(14)
C(42)-Cr(1)-C(6)	140.52(14)
C(38)-Cr(1)-C(13)	103.31(14)
C(40)-Cr(1)-C(13)	166.03(14)
C(42)-Cr(1)-C(13)	98.94(13)
C(6)-Cr(1)-C(13)	79.74(11)
C(38)-Cr(1)-C(7)	160.91(14)

C(40)-Cr(1)-C(7)	100.02(14)
C(42)-Cr(1)-C(7)	105.88(14)
C(6)-Cr(1)-C(7)	37.21(12)
C(13)-Cr(1)-C(7)	66.33(11)
C(38)-Cr(1)-C(5)	94.90(14)
C(40)-Cr(1)-C(5)	104.98(14)
C(42)-Cr(1)-C(5)	166.21(14)
C(6)-Cr(1)-C(5)	37.14(11)
C(13)-Cr(1)-C(5)	67.64(11)
C(7)-Cr(1)-C(5)	66.56(11)
C(38)-Cr(1)-C(4)	85.95(14)
C(40)-Cr(1)-C(4)	140.02(14)
C(42)-Cr(1)-C(4)	132.25(13)
C(6)-Cr(1)-C(4)	65.45(11)
C(13)-Cr(1)-C(4)	36.88(11)
C(7)-Cr(1)-C(4)	76.35(11)
C(5)-Cr(1)-C(4)	36.46(11)
C(38)-Cr(1)-C(14)	139.19(14)
C(40)-Cr(1)-C(14)	131.82(14)
C(42)-Cr(1)-C(14)	88.31(14)
C(6)-Cr(1)-C(14)	66.89(11)
C(13)-Cr(1)-C(14)	36.93(11)
C(7)-Cr(1)-C(14)	36.44(11)
C(5)-Cr(1)-C(14)	78.96(11)
C(4)-Cr(1)-C(14)	65.15(11)
C(32)-Mn(1)-C(36)	89.55(18)
C(32)-Mn(1)-C(34)	88.31(18)
C(36)-Mn(1)-C(34)	91.52(17)
C(32)-Mn(1)-C(2)	89.75(16)
C(36)-Mn(1)-C(2)	140.19(16)
C(34)-Mn(1)-C(2)	128.23(15)
C(32)-Mn(1)-C(1)	101.34(17)
C(36)-Mn(1)-C(1)	102.86(16)
C(34)-Mn(1)-C(1)	162.62(15)
C(2)-Mn(1)-C(1)	38.70(13)
C(32)-Mn(1)-C(3)	114.96(16)
C(36)-Mn(1)-C(3)	153.75(15)
C(34)-Mn(1)-C(3)	98.13(14)
C(2)-Mn(1)-C(3)	38.49(12)
C(1)-Mn(1)-C(3)	64.74(13)
C(32)-Mn(1)-C(17)	139.06(17)
C(36)-Mn(1)-C(17)	91.76(15)
C(34)-Mn(1)-C(17)	132.52(14)
C(2)-Mn(1)-C(17)	64.22(13)
C(1)-Mn(1)-C(17)	38.78(12)
C(3)-Mn(1)-C(17)	63.83(13)
C(32)-Mn(1)-C(12)	151.91(16)
C(36)-Mn(1)-C(12)	116.20(14)
C(34)-Mn(1)-C(12)	101.25(13)
C(2)-Mn(1)-C(12)	63.52(12)
C(1)-Mn(1)-C(12)	63.75(12)
C(3)-Mn(1)-C(12)	37.97(11)
C(17)-Mn(1)-C(12)	37.29(12)
C(2)-C(1)-C(17)	107.1(3)
C(2)-C(1)-Mn(1)	70.1(2)
C(17)-C(1)-Mn(1)	72.47(19)
C(3)-C(2)-C(1)	108.9(3)
C(3)-C(2)-Mn(1)	71.69(19)
C(1)-C(2)-Mn(1)	71.17(19)
C(2)-C(3)-C(12)	108.3(3)

C(2)-C(3)-Mn(1)	69.82(19)
C(12)-C(3)-Mn(1)	74.67(18)
O(18)-C(4)-C(5)	118.7(3)
O(18)-C(4)-C(13)	118.8(3)
C(5)-C(4)-C(13)	122.5(3)
O(18)-C(4)-Cr(1)	133.5(2)
C(5)-C(4)-Cr(1)	70.59(17)
C(13)-C(4)-Cr(1)	69.71(17)
C(4)-C(5)-C(6)	117.7(3)
C(4)-C(5)-C(26)	121.4(3)
C(6)-C(5)-C(26)	120.8(3)
C(4)-C(5)-Cr(1)	72.95(17)
C(6)-C(5)-Cr(1)	70.11(17)
C(26)-C(5)-Cr(1)	129.7(2)
C(7)-C(6)-C(5)	120.0(3)
C(7)-C(6)-C(28)	118.3(3)
C(5)-C(6)-C(28)	121.3(3)
C(7)-C(6)-Cr(1)	72.31(17)
C(5)-C(6)-Cr(1)	72.75(17)
C(28)-C(6)-Cr(1)	133.5(2)
O(30)-C(7)-C(6)	115.4(3)
O(30)-C(7)-C(14)	121.9(3)
C(6)-C(7)-C(14)	122.6(3)
O(30)-C(7)-Cr(1)	131.7(2)
C(6)-C(7)-Cr(1)	70.48(17)
C(14)-C(7)-Cr(1)	74.64(17)
C(9)-C(8)-C(15)	121.9(3)
C(8)-C(9)-C(10)	120.5(3)
C(11)-C(10)-C(9)	119.3(3)
C(10)-C(11)-C(16)	121.0(3)
C(17)-C(12)-C(3)	107.1(3)
C(17)-C(12)-C(13)	119.6(3)
C(3)-C(12)-C(13)	132.8(3)
C(17)-C(12)-Mn(1)	69.14(17)
C(3)-C(12)-Mn(1)	67.36(17)
C(13)-C(12)-Mn(1)	134.6(2)
C(4)-C(13)-C(14)	119.1(3)
C(4)-C(13)-C(12)	121.5(3)
C(14)-C(13)-C(12)	119.0(3)
C(4)-C(13)-Cr(1)	73.42(17)
C(14)-C(13)-Cr(1)	74.63(17)
C(12)-C(13)-Cr(1)	129.3(2)
C(7)-C(14)-C(13)	117.1(3)
C(7)-C(14)-C(15)	123.3(3)
C(13)-C(14)-C(15)	119.4(3)
C(7)-C(14)-Cr(1)	68.92(17)
C(13)-C(14)-Cr(1)	68.44(17)
C(15)-C(14)-Cr(1)	138.5(2)
C(16)-C(15)-C(8)	116.4(3)
C(16)-C(15)-C(14)	120.0(3)
C(8)-C(15)-C(14)	123.2(3)
C(11)-C(16)-C(15)	120.7(3)
C(11)-C(16)-C(17)	119.6(3)
C(15)-C(16)-C(17)	119.7(3)
C(12)-C(17)-C(1)	108.5(3)
C(12)-C(17)-C(16)	121.5(3)
C(1)-C(17)-C(16)	130.0(3)
C(12)-C(17)-Mn(1)	73.57(18)
C(1)-C(17)-Mn(1)	68.75(19)
C(16)-C(17)-Mn(1)	125.7(2)

C(4)-O(18)-Si(19)	124.8(2)
O(18)-Si(19)-C(21)	111.27(16)
O(18)-Si(19)-C(20)	110.85(17)
C(21)-Si(19)-C(20)	105.8(2)
O(18)-Si(19)-C(22)	102.95(16)
C(21)-Si(19)-C(22)	113.38(19)
C(20)-Si(19)-C(22)	112.7(2)
C(25)-C(22)-C(24)	108.5(4)
C(25)-C(22)-C(23)	109.0(4)
C(24)-C(22)-C(23)	110.8(4)
C(25)-C(22)-Si(19)	110.6(3)
C(24)-C(22)-Si(19)	110.4(3)
C(23)-C(22)-Si(19)	107.6(3)
C(5)-C(26)-C(27)	116.4(3)
C(6)-C(28)-C(29)	110.0(3)
C(7)-O(30)-C(31)	116.5(2)
O(33)-C(32)-Mn(1)	179.3(4)
O(35)-C(34)-Mn(1)	176.7(3)
O(37)-C(36)-Mn(1)	178.3(4)
O(39)-C(38)-Cr(1)	177.0(3)
O(41)-C(40)-Cr(1)	179.4(4)
O(43)-C(42)-Cr(1)	178.4(3)
Cl(2)-C-Cl(1)	111.3(4)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **18**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Cr(1)	26(1)	28(1)	23(1)	0(1)	3(1)	-2(1)
Mn(1)	32(1)	35(1)	24(1)	1(1)	7(1)	0(1)
C(1)	44(2)	36(2)	27(2)	-6(2)	8(2)	-5(2)
C(2)	38(2)	45(2)	22(2)	1(2)	1(1)	-4(2)
C(3)	30(2)	36(2)	24(2)	2(1)	4(1)	-2(2)
C(4)	24(2)	29(2)	24(2)	4(1)	3(1)	-2(1)
C(5)	25(2)	33(2)	25(2)	1(1)	6(1)	1(1)
C(6)	25(2)	36(2)	21(2)	-1(1)	5(1)	-4(1)
C(7)	27(2)	29(2)	21(2)	5(1)	1(1)	-4(1)
C(8)	36(2)	32(2)	31(2)	1(2)	1(1)	1(2)
C(9)	42(2)	30(2)	42(2)	1(2)	-8(2)	5(2)
C(10)	48(2)	29(2)	49(2)	-8(2)	0(2)	7(2)
C(11)	49(2)	35(2)	34(2)	-8(2)	6(2)	3(2)
C(12)	24(2)	28(2)	23(2)	1(1)	3(1)	-1(1)
C(13)	22(2)	27(2)	22(2)	0(1)	0(1)	-6(1)
C(14)	22(2)	26(2)	26(2)	0(1)	3(1)	-3(1)
C(15)	22(2)	28(2)	27(2)	0(1)	2(1)	-4(1)
C(16)	29(2)	28(2)	32(2)	0(1)	3(1)	-3(1)
C(17)	34(2)	29(2)	24(2)	-2(1)	4(1)	-3(1)
O(18)	27(1)	34(1)	25(1)	5(1)	2(1)	6(1)
Si(19)	26(1)	46(1)	32(1)	7(1)	2(1)	1(1)
C(20)	46(2)	74(3)	72(3)	-19(3)	3(2)	-17(2)
C(21)	38(2)	76(3)	56(3)	23(2)	10(2)	-3(2)
C(22)	43(2)	66(3)	40(2)	22(2)	3(2)	14(2)
C(23)	39(3)	143(6)	100(4)	59(4)	-9(3)	21(3)

C(24)	121(5)	61(3)	69(3)	19(3)	10(3)	44(3)
C(25)	65(3)	81(3)	53(3)	31(2)	10(2)	9(3)
C(26)	41(2)	46(2)	30(2)	2(2)	9(2)	12(2)
C(27)	78(3)	39(2)	76(3)	-6(2)	31(3)	12(2)
C(28)	35(2)	45(2)	22(2)	-1(2)	5(1)	1(2)
C(29)	52(2)	77(3)	39(2)	6(2)	19(2)	-11(2)
O(30)	37(1)	35(1)	25(1)	8(1)	2(1)	3(1)
C(31)	42(2)	48(2)	40(2)	4(2)	-16(2)	5(2)
C(32)	49(2)	66(3)	40(2)	1(2)	14(2)	-4(2)
O(33)	96(3)	127(3)	41(2)	13(2)	34(2)	-22(2)
C(34)	34(2)	43(2)	37(2)	5(2)	11(2)	-1(2)
O(35)	59(2)	41(2)	68(2)	-6(2)	16(2)	-12(1)
C(36)	42(2)	46(2)	44(2)	2(2)	10(2)	-3(2)
O(37)	39(2)	70(2)	84(2)	7(2)	2(2)	11(2)
C(38)	43(2)	35(2)	40(2)	2(2)	14(2)	-1(2)
O(39)	90(2)	44(2)	74(2)	23(2)	33(2)	10(2)
C(40)	44(2)	39(2)	34(2)	-2(2)	6(2)	-7(2)
O(41)	79(2)	66(2)	43(2)	-17(2)	-9(2)	-18(2)
C(42)	34(2)	41(2)	31(2)	0(2)	-3(2)	-3(2)
O(43)	30(1)	89(2)	54(2)	0(2)	9(1)	4(2)
C	173(8)	97(6)	263(12)	-92(7)	122(9)	-60(6)
Cl(1)	178(2)	131(2)	118(2)	29(1)	34(1)	69(2)
Cl(2)	114(2)	299(4)	139(2)	-74(2)	-21(1)	73(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **18**.

	x	y	z	U(eq)
H(1)	7740	5188	2970	42
H(2)	8817	3820	3374	42
H(3)	9105	2858	2443	36
H(8)	6910	5738	59	40
H(9)	6099	7002	415	47
H(10)	5944	7195	1491	51
H(11)	6745	6158	2214	47
H(20A)	10928	4322	2088	96
H(20B)	12217	4053	2367	96
H(20C)	11136	3660	2672	96
H(21A)	12291	2757	791	84
H(21B)	12926	3497	1236	84
H(21C)	11731	3711	812	84
H(23A)	13311	2518	2621	143
H(23B)	13663	2085	1988	143
H(23C)	13531	1487	2591	143
H(24A)	12055	547	1853	126
H(24B)	12228	1203	1288	126
H(24C)	10959	1027	1479	126
H(25A)	11652	1136	2905	99
H(25B)	10475	1489	2525	99
H(25C)	11298	2143	2958	99
H(26A)	10698	2021	527	46
H(26B)	10599	2402	-174	46
H(27A)	9137	1056	232	94
H(27B)	10111	915	-229	94

H(27C)	8968	1462	-463	94
H(28A)	8141	3489	-1086	41
H(28B)	9102	2748	-915	41
H(29A)	9583	4590	-913	82
H(29B)	9939	3915	-1430	82
H(29C)	10547	3862	-718	82
H(31A)	6222	3904	-845	68
H(31B)	5997	4928	-955	68
H(31C)	5842	4497	-287	68
H(1B1)	6249	10318	-58	204
H(1B2)	7186	10077	-524	204

2.7 *Anti*-tricarbonyl-{tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (19)

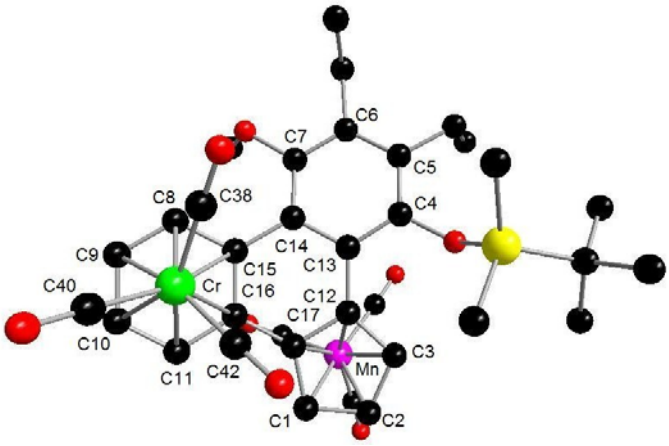


Table 1. Crystal data and structure refinement for **19**.

Empirical formula	C_{34} H_{35} Cr Mn O_8 Si
Formula weight	706.65
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c (No. 15)
Unit cell dimensions	a = 28.566(1) Å α = 90°. b = 17.145(1) Å β = 102.08(1)°. c = 14.458(1) Å γ = 90°.
Volume	6924.2(7) Å^3
Z, Calculated density	8, 1.356 Mg/m^3
Absorption coefficient	0.761 mm^{-1}
F(000)	2928
Crystal size	0.30 x 0.06 x 0.03 mm

Theta range for data collection 1.46 to 27.93°.

Limiting indices -37<=h<=30, -22<=k<=20, -15<=l<=18

Reflections collected / unique 27349 / 8100 [R(int) = 0.1110]

Completeness to theta = 27.93 97.4 %

Max. and min. transmission 0.9775 and 0.8040

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 4779 / 0 / 414

Goodness-of-fit on F^2 1.057

Final R indices [I>2σ(I)] R1 = 0.0723, wR^2 = 0.0933

R indices (all data) R1 = 0.1548, wR^2 = 0.1113

Largest diff. peak and hole 0.399 and -0.536 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **19**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mn(1)	783(1)	218(1)	1602(1)	31(1)
Cr(1)	2504(1)	1082(1)	3542(1)	32(1)
C(1)	1481(1)	-214(2)	1563(2)	36(1)
C(2)	1234(1)	-23(2)	638(2)	37(1)
C(3)	1122(1)	775(2)	601(2)	33(1)
C(4)	1092(1)	2520(2)	1343(2)	27(1)
C(5)	978(1)	3220(2)	1741(2)	31(1)
C(6)	1086(1)	3295(2)	2725(2)	32(1)
C(7)	1315(1)	2691(2)	3280(2)	30(1)
C(8)	2009(1)	1515(2)	4391(2)	34(1)
C(9)	2283(1)	930(3)	4908(2)	41(1)
C(10)	2314(1)	191(3)	4513(2)	42(1)
C(11)	2058(1)	37(2)	3605(2)	36(1)
C(12)	1314(1)	1106(2)	1512(2)	27(1)
C(13)	1289(1)	1890(2)	1902(2)	26(1)
C(14)	1439(1)	1992(2)	2891(2)	27(1)
C(15)	1727(1)	1377(2)	3466(2)	27(1)
C(16)	1768(1)	625(2)	3075(2)	28(1)
C(17)	1527(1)	485(2)	2098(2)	28(1)
O(18)	995(1)	2446(1)	371(1)	30(1)
Si(19)	1376(1)	2696(1)	-313(1)	33(1)
C(20)	1818(2)	1905(3)	-337(3)	64(1)
C(21)	1725(1)	3571(2)	167(3)	48(1)
C(22)	986(1)	2845(3)	-1514(2)	45(1)

C(23)	623(2)	3496(3)	-1503(3)	74(2)
C(24)	1298(2)	3068(3)	-2216(3)	71(2)
C(25)	718(2)	2088(3)	-1849(3)	89(2)
C(26)	705(1)	3845(2)	1111(3)	42(1)
C(27)	168(2)	3709(3)	948(3)	82(2)
C(28)	1006(1)	4054(2)	3202(3)	44(1)
C(29)	1447(2)	4575(2)	3300(3)	66(1)
O(30)	1420(1)	2808(2)	4250(2)	38(1)
C(31)	1080(2)	2457(3)	4720(3)	55(1)
C(32)	404(2)	-580(3)	1133(3)	48(1)
O(33)	175(1)	-1108(2)	835(2)	79(1)
C(34)	302(2)	916(3)	1428(3)	46(1)
O(35)	11(1)	1381(2)	1330(2)	74(1)
C(36)	713(1)	20(2)	2772(3)	39(1)
O(37)	673(1)	-100(2)	3533(2)	63(1)
C(38)	2667(2)	2102(3)	3380(3)	48(1)
O(39)	2760(1)	2745(2)	3272(3)	80(1)
C(40)	3142(2)	850(2)	3980(3)	43(1)
O(41)	3540(1)	700(2)	4232(2)	63(1)
C(42)	2581(1)	883(2)	2344(3)	40(1)
O(43)	2613(1)	759(2)	1575(2)	65(1)

Table 3. Bond lengths [Å] and angles [°] for **19**.

Mn(1)-C(36)	1.778(4)
Mn(1)-C(32)	1.789(4)
Mn(1)-C(34)	1.800(5)
Mn(1)-C(2)	2.126(4)
Mn(1)-C(3)	2.128(3)
Mn(1)-C(1)	2.138(4)
Mn(1)-C(17)	2.146(3)
Mn(1)-C(12)	2.171(3)
Cr(1)-C(42)	1.823(4)
Cr(1)-C(38)	1.838(5)
Cr(1)-C(40)	1.843(4)
Cr(1)-C(8)	2.190(3)
Cr(1)-C(11)	2.211(4)
Cr(1)-C(9)	2.212(3)
Cr(1)-C(16)	2.213(3)
Cr(1)-C(10)	2.218(4)
Cr(1)-C(15)	2.257(3)
C(1)-C(2)	1.414(5)
C(1)-C(17)	1.418(5)
C(2)-C(3)	1.404(5)
C(3)-C(12)	1.434(4)
C(4)-O(18)	1.380(4)
C(4)-C(13)	1.395(4)
C(4)-C(5)	1.398(5)
C(5)-C(6)	1.398(5)
C(5)-C(26)	1.511(5)
C(6)-C(7)	1.388(5)
C(6)-C(28)	1.511(5)
C(7)-O(30)	1.386(4)
C(7)-C(14)	1.399(5)
C(8)-C(9)	1.392(5)
C(8)-C(15)	1.429(4)
C(9)-C(10)	1.399(5)

C(10)-C(11)	1.388(5)
C(11)-C(16)	1.423(5)
C(12)-C(17)	1.417(5)
C(12)-C(13)	1.465(5)
C(13)-C(14)	1.415(4)
C(14)-C(15)	1.482(5)
C(15)-C(16)	1.422(5)
C(16)-C(17)	1.455(4)
O(18)-Si(19)	1.673(2)
Si(19)-C(21)	1.855(4)
Si(19)-C(20)	1.859(4)
Si(19)-C(22)	1.874(4)
C(22)-C(23)	1.527(6)
C(22)-C(24)	1.531(5)
C(22)-C(25)	1.534(6)
C(26)-C(27)	1.520(5)
C(28)-C(29)	1.525(5)
O(30)-C(31)	1.429(4)
C(32)-O(33)	1.147(5)
C(34)-O(35)	1.138(5)
C(36)-O(37)	1.148(4)
C(38)-O(39)	1.151(5)
C(40)-O(41)	1.148(4)
C(42)-O(43)	1.154(4)
C(36)-Mn(1)-C(32)	91.99(17)
C(36)-Mn(1)-C(34)	91.47(17)
C(32)-Mn(1)-C(34)	94.10(19)
C(36)-Mn(1)-C(2)	142.28(16)
C(32)-Mn(1)-C(2)	90.29(16)
C(34)-Mn(1)-C(2)	125.91(16)
C(36)-Mn(1)-C(3)	152.96(15)
C(32)-Mn(1)-C(3)	114.29(15)
C(34)-Mn(1)-C(3)	92.77(16)
C(2)-Mn(1)-C(3)	38.53(13)
C(36)-Mn(1)-C(1)	104.47(15)
C(32)-Mn(1)-C(1)	102.68(17)
C(34)-Mn(1)-C(1)	156.25(16)
C(2)-Mn(1)-C(1)	38.75(13)
C(3)-Mn(1)-C(1)	65.10(14)
C(36)-Mn(1)-C(17)	91.32(14)
C(32)-Mn(1)-C(17)	140.32(17)
C(34)-Mn(1)-C(17)	125.33(16)
C(2)-Mn(1)-C(17)	64.39(13)
C(3)-Mn(1)-C(17)	64.68(13)
C(1)-Mn(1)-C(17)	38.67(13)
C(36)-Mn(1)-C(12)	114.17(15)
C(32)-Mn(1)-C(12)	152.77(15)
C(34)-Mn(1)-C(12)	92.69(16)
C(2)-Mn(1)-C(12)	64.62(13)
C(3)-Mn(1)-C(12)	38.96(12)
C(1)-Mn(1)-C(12)	64.87(14)
C(17)-Mn(1)-C(12)	38.31(12)
C(42)-Cr(1)-C(38)	88.44(18)
C(42)-Cr(1)-C(40)	88.86(16)
C(38)-Cr(1)-C(40)	89.51(19)
C(42)-Cr(1)-C(8)	144.74(15)
C(38)-Cr(1)-C(8)	87.61(16)
C(40)-Cr(1)-C(8)	126.11(14)
C(42)-Cr(1)-C(11)	94.18(15)
C(38)-Cr(1)-C(11)	159.97(16)

C(40)-Cr(1)-C(11)	110.38(16)
C(8)-Cr(1)-C(11)	78.80(14)
C(42)-Cr(1)-C(9)	160.09(17)
C(38)-Cr(1)-C(9)	110.67(17)
C(40)-Cr(1)-C(9)	96.56(15)
C(8)-Cr(1)-C(9)	36.86(13)
C(11)-Cr(1)-C(9)	65.97(14)
C(42)-Cr(1)-C(16)	86.51(14)
C(38)-Cr(1)-C(16)	123.14(16)
C(40)-Cr(1)-C(16)	146.82(16)
C(8)-Cr(1)-C(16)	66.81(13)
C(11)-Cr(1)-C(16)	37.53(12)
C(9)-Cr(1)-C(16)	78.46(13)
C(42)-Cr(1)-C(10)	124.58(17)
C(38)-Cr(1)-C(10)	146.94(16)
C(40)-Cr(1)-C(10)	89.45(16)
C(8)-Cr(1)-C(10)	66.74(14)
C(11)-Cr(1)-C(10)	36.52(13)
C(9)-Cr(1)-C(10)	36.81(14)
C(16)-Cr(1)-C(10)	66.80(13)
C(42)-Cr(1)-C(15)	107.93(14)
C(38)-Cr(1)-C(15)	92.99(16)
C(40)-Cr(1)-C(15)	163.08(14)
C(8)-Cr(1)-C(15)	37.45(11)
C(11)-Cr(1)-C(15)	67.30(13)
C(9)-Cr(1)-C(15)	66.92(12)
C(16)-Cr(1)-C(15)	37.08(12)
C(10)-Cr(1)-C(15)	79.37(13)
C(2)-C(1)-C(17)	106.9(3)
C(2)-C(1)-Mn(1)	70.2(2)
C(17)-C(1)-Mn(1)	71.0(2)
C(3)-C(2)-C(1)	109.1(3)
C(3)-C(2)-Mn(1)	70.8(2)
C(1)-C(2)-Mn(1)	71.1(2)
C(2)-C(3)-C(12)	108.1(3)
C(2)-C(3)-Mn(1)	70.6(2)
C(12)-C(3)-Mn(1)	72.15(18)
O(18)-C(4)-C(13)	119.3(3)
O(18)-C(4)-C(5)	118.9(3)
C(13)-C(4)-C(5)	121.8(3)
C(6)-C(5)-C(4)	118.5(3)
C(6)-C(5)-C(26)	121.6(3)
C(4)-C(5)-C(26)	119.7(3)
C(7)-C(6)-C(5)	119.7(3)
C(7)-C(6)-C(28)	118.5(3)
C(5)-C(6)-C(28)	121.4(3)
O(30)-C(7)-C(6)	116.9(3)
O(30)-C(7)-C(14)	120.7(3)
C(6)-C(7)-C(14)	122.4(3)
C(9)-C(8)-C(15)	121.7(4)
C(9)-C(8)-Cr(1)	72.4(2)
C(15)-C(8)-Cr(1)	73.83(18)
C(8)-C(9)-C(10)	120.7(3)
C(8)-C(9)-Cr(1)	70.72(19)
C(10)-C(9)-Cr(1)	71.8(2)
C(11)-C(10)-C(9)	119.6(3)
C(11)-C(10)-Cr(1)	71.5(2)
C(9)-C(10)-Cr(1)	71.4(2)
C(10)-C(11)-C(16)	120.4(4)
C(10)-C(11)-Cr(1)	72.0(2)

C(16)-C(11)-Cr(1)	71.3(2)
C(17)-C(12)-C(3)	106.6(3)
C(17)-C(12)-C(13)	120.6(3)
C(3)-C(12)-C(13)	132.6(3)
C(17)-C(12)-Mn(1)	69.87(19)
C(3)-C(12)-Mn(1)	68.89(19)
C(13)-C(12)-Mn(1)	122.1(2)
C(4)-C(13)-C(14)	119.3(3)
C(4)-C(13)-C(12)	122.2(3)
C(14)-C(13)-C(12)	118.3(3)
C(7)-C(14)-C(13)	117.6(3)
C(7)-C(14)-C(15)	122.8(3)
C(13)-C(14)-C(15)	119.6(3)
C(16)-C(15)-C(8)	116.5(3)
C(16)-C(15)-C(14)	120.3(3)
C(8)-C(15)-C(14)	123.0(3)
C(16)-C(15)-Cr(1)	69.75(18)
C(8)-C(15)-Cr(1)	68.72(18)
C(14)-C(15)-Cr(1)	127.8(2)
C(15)-C(16)-C(11)	121.0(3)
C(15)-C(16)-C(17)	118.3(3)
C(11)-C(16)-C(17)	120.6(3)
C(15)-C(16)-Cr(1)	73.18(19)
C(11)-C(16)-Cr(1)	71.18(19)
C(17)-C(16)-Cr(1)	125.5(2)
C(12)-C(17)-C(1)	109.2(3)
C(12)-C(17)-C(16)	120.9(3)
C(1)-C(17)-C(16)	129.8(3)
C(12)-C(17)-Mn(1)	71.82(19)
C(1)-C(17)-Mn(1)	70.35(19)
C(16)-C(17)-Mn(1)	126.5(2)
C(4)-O(18)-Si(19)	124.1(2)
O(18)-Si(19)-C(21)	110.59(15)
O(18)-Si(19)-C(20)	110.75(16)
C(21)-Si(19)-C(20)	106.4(2)
O(18)-Si(19)-C(22)	104.45(15)
C(21)-Si(19)-C(22)	113.87(18)
C(20)-Si(19)-C(22)	110.9(2)
C(23)-C(22)-C(24)	108.4(4)
C(23)-C(22)-C(25)	109.0(4)
C(24)-C(22)-C(25)	108.9(4)
C(23)-C(22)-Si(19)	111.3(3)
C(24)-C(22)-Si(19)	109.5(3)
C(25)-C(22)-Si(19)	109.7(3)
C(5)-C(26)-C(27)	111.2(3)
C(6)-C(28)-C(29)	110.3(3)
C(7)-O(30)-C(31)	113.3(3)
O(33)-C(32)-Mn(1)	177.5(4)
O(35)-C(34)-Mn(1)	177.3(4)
O(37)-C(36)-Mn(1)	179.0(4)
O(39)-C(38)-Cr(1)	178.8(4)
O(41)-C(40)-Cr(1)	178.4(3)
O(43)-C(42)-Cr(1)	177.7(3)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **19**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn(1)	36(1)	30(1)	26(1)	2(1)	2(1)	-5(1)
Cr(1)	31(1)	37(1)	26(1)	-2(1)	4(1)	3(1)
C(1)	42(2)	25(2)	41(2)	-2(2)	11(2)	0(2)
C(2)	52(2)	29(2)	32(2)	-8(2)	11(2)	-8(2)
C(3)	45(2)	31(2)	23(2)	-1(2)	7(2)	-4(2)
C(4)	25(2)	29(2)	27(2)	1(2)	3(1)	-3(2)
C(5)	29(2)	26(2)	38(2)	2(2)	7(2)	-1(2)
C(6)	29(2)	30(2)	37(2)	-7(2)	9(2)	2(2)
C(7)	30(2)	33(2)	26(2)	-6(2)	4(1)	-4(2)
C(8)	32(2)	44(3)	26(2)	-2(2)	7(2)	8(2)
C(9)	39(2)	63(3)	21(2)	4(2)	6(2)	11(2)
C(10)	41(2)	50(3)	34(2)	12(2)	9(2)	12(2)
C(11)	38(2)	31(2)	39(2)	6(2)	11(2)	3(2)
C(12)	30(2)	26(2)	24(2)	1(2)	6(1)	-6(2)
C(13)	25(2)	24(2)	28(2)	-2(2)	4(1)	-2(2)
C(14)	27(2)	28(2)	27(2)	-3(2)	4(1)	-2(2)
C(15)	24(2)	35(2)	22(2)	0(2)	4(1)	3(2)
C(16)	24(2)	29(2)	31(2)	5(2)	6(1)	0(2)
C(17)	30(2)	29(2)	27(2)	1(2)	8(2)	-2(2)
O(18)	33(1)	31(2)	26(1)	3(1)	5(1)	-4(1)
Si(19)	34(1)	32(1)	34(1)	4(1)	8(1)	-5(1)
C(20)	61(3)	57(3)	83(3)	12(3)	40(3)	8(3)
C(21)	44(2)	52(3)	46(2)	-3(2)	6(2)	-17(2)
C(22)	50(3)	53(3)	31(2)	3(2)	6(2)	-18(2)
C(23)	56(3)	106(5)	53(3)	27(3)	-6(2)	5(3)
C(24)	83(4)	93(4)	41(2)	12(3)	21(2)	-20(3)
C(25)	109(4)	89(4)	58(3)	-4(3)	-8(3)	-55(4)
C(26)	45(2)	36(3)	45(2)	6(2)	7(2)	12(2)
C(27)	44(3)	117(5)	83(4)	34(3)	9(2)	31(3)
C(28)	46(2)	38(3)	47(2)	-6(2)	9(2)	11(2)
C(29)	74(3)	33(3)	86(3)	-19(2)	8(3)	-6(2)
O(30)	42(2)	43(2)	29(1)	-12(1)	6(1)	2(1)
C(31)	62(3)	69(3)	39(2)	0(2)	22(2)	9(3)
C(32)	51(3)	55(3)	37(2)	-3(2)	5(2)	-13(2)
O(33)	88(3)	75(3)	71(2)	-20(2)	9(2)	-47(2)
C(34)	41(2)	51(3)	44(2)	11(2)	6(2)	-7(2)
O(35)	58(2)	76(3)	86(2)	25(2)	17(2)	29(2)
C(36)	35(2)	41(3)	37(2)	3(2)	2(2)	-2(2)
O(37)	68(2)	88(3)	34(2)	12(2)	15(1)	1(2)
C(38)	51(3)	49(3)	47(2)	-1(2)	19(2)	-2(2)
O(39)	102(3)	41(2)	107(3)	-4(2)	48(2)	-13(2)
C(40)	41(2)	50(3)	37(2)	-3(2)	8(2)	3(2)
O(41)	35(2)	83(3)	66(2)	1(2)	0(1)	11(2)
C(42)	30(2)	56(3)	35(2)	-5(2)	7(2)	-7(2)
O(43)	53(2)	106(3)	38(2)	-18(2)	16(1)	-9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **19**.

	x	y	z	U(eq)

H(1)	1593	-710	1782	43
H(2)	1157	-374	129	44
H(3)	951	1046	71	39
H(8)	2008	2015	4658	41
H(9)	2450	1031	5529	49
H(10)	2506	-198	4860	50
H(11)	2077	-459	3338	43
H(20A)	1989	1794	302	95
H(20B)	2044	2070	-715	95
H(20C)	1653	1439	-612	95
H(21A)	1513	4017	123	72
H(21B)	1969	3672	-195	72
H(21C)	1877	3482	824	72
H(23A)	442	3586	-2140	111
H(23B)	789	3970	-1260	111
H(23C)	406	3345	-1100	111
H(24A)	1525	2654	-2245	107
H(24B)	1469	3547	-2009	107
H(24C)	1096	3146	-2838	107
H(25A)	516	1946	-1412	134
H(25B)	947	1674	-1870	134
H(25C)	521	2165	-2475	134
H(26A)	804	3845	502	51
H(26B)	782	4356	1406	51
H(27A)	91	3208	643	123
H(27B)	2	4119	546	123
H(27C)	69	3715	1550	123
H(28A)	941	3947	3829	53
H(28B)	727	4323	2827	53
H(29A)	1723	4305	3666	99
H(29B)	1394	5054	3620	99
H(29C)	1504	4695	2678	99
H(31A)	762	2647	4442	83
H(31B)	1159	2592	5386	83
H(31C)	1089	1895	4651	83

2.8 *Syn*-tricarbonyl-{tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}manganese (20)

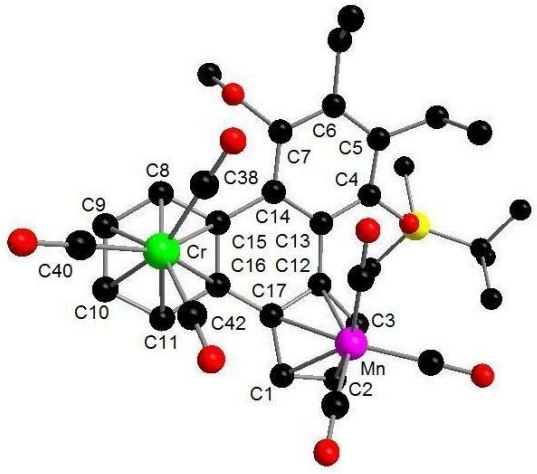


Table 1. Crystal data and structure refinement for **20**.

Empirical formula	C_{34} H_{35} Cr Mn O_8 Si
Formula weight	706.65
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P1bar (No. 2)
Unit cell dimensions	a = 7.372(1) Å α = 96.46(1)°. b = 14.481(1) Å β = 91.20(1)°. c = 15.609(1) Å γ = 98.64(1)°.
Volume	1635.7(3) $Å^3$
Z, Calculated density	2, 1.435 Mg/m^3
Absorption coefficient	0.805 mm^{-1}
F(000)	732
Crystal size	0.54 x 0.45 x 0.40 mm
Theta range for data collection	2.63 to 30.89°.
Limiting indices	0<=h<=10, -20<=k<=20, -22<=l<=21
Reflections collected / unique	19093 / 9994 [R(int) = 0.042]
Completeness to theta = 30.89	96.6 %
Max. and min. transmission	0.7390 and 0.6704
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7795 / 0 / 414
Goodness-of-fit on F^2	1.049
Final R indices [I>2σ(I)]	R1 = 0.0448, wR^2 = 0.1127
R indices (all data)	R1 = 0.0625, wR^2 = 0.1217
Largest diff. peak and hole	0.495 and -0.615 $eÅ^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **20**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

x	y	z	U(eq)

Mn(1)	1644(1)	7196(1)	954(1)	25(1)
Cr(1)	5498(1)	9906(1)	1960(1)	26(1)
C(1)	4113(3)	7202(1)	251(1)	32(1)
C(2)	3186(3)	6274(1)	221(1)	34(1)
C(3)	3064(3)	6037(1)	1080(1)	28(1)
C(4)	3332(3)	6359(1)	3121(1)	22(1)
C(5)	3102(3)	6632(1)	3993(1)	24(1)
C(6)	4072(3)	7487(1)	4373(1)	26(1)
C(7)	5204(3)	8054(1)	3870(1)	24(1)
C(8)	7505(3)	9331(1)	2724(2)	32(1)
C(9)	8459(3)	9907(2)	2163(2)	37(1)
C(10)	8055(3)	9759(2)	1274(2)	36(1)
C(11)	6702(3)	9021(1)	952(1)	32(1)
C(12)	3962(3)	6813(1)	1649(1)	23(1)
C(13)	4221(3)	6993(1)	2588(1)	21(1)
C(14)	5215(3)	7863(1)	2967(1)	23(1)
C(15)	6177(3)	8533(1)	2405(1)	25(1)
C(16)	5803(3)	8383(1)	1501(1)	26(1)
C(17)	4608(3)	7543(1)	1130(1)	25(1)
O(18)	2495(2)	5487(1)	2761(1)	24(1)
Si(19)	3376(1)	4481(1)	2745(1)	24(1)
C(20)	5097(4)	4414(2)	1899(2)	44(1)
C(21)	4583(4)	4407(2)	3787(2)	45(1)
C(22)	1307(3)	3549(1)	2500(1)	30(1)
C(23)	-12(4)	3567(2)	3241(2)	54(1)
C(24)	1907(5)	2577(2)	2351(2)	58(1)
C(25)	282(4)	3722(2)	1681(2)	46(1)
C(26)	1665(3)	6032(2)	4453(1)	33(1)
C(27)	-249(4)	6183(2)	4201(2)	51(1)
C(28)	3872(3)	7852(2)	5312(1)	32(1)
C(29)	2522(4)	8540(2)	5420(2)	51(1)
O(30)	6218(2)	8863(1)	4296(1)	30(1)
C(31)	7941(3)	8703(2)	4646(2)	39(1)
C(32)	762(3)	7941(2)	254(1)	35(1)
O(33)	153(3)	8364(1)	-224(1)	52(1)
C(34)	-512(4)	6444(2)	845(2)	45(1)
O(35)	-1887(3)	5950(2)	762(2)	79(1)
C(36)	996(3)	7827(2)	1927(2)	39(1)
O(37)	640(3)	8193(2)	2575(1)	65(1)
C(38)	4018(3)	10066(2)	2888(2)	40(1)
O(39)	3073(3)	10173(2)	3453(1)	68(1)
C(40)	5969(3)	11179(2)	1959(2)	47(1)
O(41)	6250(3)	11981(1)	1941(2)	80(1)
C(42)	3494(3)	9954(1)	1267(1)	32(1)
O(43)	2242(3)	10036(2)	841(1)	52(1)

Table 3. Bond lengths [Å] and angles [°] for **20**.

Mn(1)-C(34)	1.780(3)
Mn(1)-C(36)	1.795(2)
Mn(1)-C(32)	1.796(2)
Mn(1)-C(3)	2.131(2)
Mn(1)-C(2)	2.133(2)
Mn(1)-C(1)	2.145(2)
Mn(1)-C(17)	2.172(2)
Mn(1)-C(12)	2.179(2)

Cr(1)-C(40)	1.824(2)
Cr(1)-C(42)	1.827(2)
Cr(1)-C(38)	1.846(2)
Cr(1)-C(8)	2.197(2)
Cr(1)-C(9)	2.199(2)
Cr(1)-C(11)	2.204(2)
Cr(1)-C(10)	2.214(2)
Cr(1)-C(16)	2.2868(19)
Cr(1)-C(15)	2.2982(18)
C(1)-C(2)	1.408(3)
C(1)-C(17)	1.426(3)
C(2)-C(3)	1.422(3)
C(3)-C(12)	1.420(3)
C(4)-O(18)	1.372(2)
C(4)-C(5)	1.395(2)
C(4)-C(13)	1.406(2)
C(5)-C(6)	1.396(3)
C(5)-C(26)	1.513(3)
C(6)-C(7)	1.397(3)
C(6)-C(28)	1.519(3)
C(7)-O(30)	1.384(2)
C(7)-C(14)	1.406(3)
C(8)-C(9)	1.404(3)
C(8)-C(15)	1.432(3)
C(9)-C(10)	1.399(4)
C(10)-C(11)	1.388(3)
C(11)-C(16)	1.430(3)
C(12)-C(17)	1.433(2)
C(12)-C(13)	1.464(2)
C(13)-C(14)	1.418(2)
C(14)-C(15)	1.492(2)
C(15)-C(16)	1.419(3)
C(16)-C(17)	1.446(3)
O(18)-Si(19)	1.6793(14)
Si(19)-C(20)	1.855(2)
Si(19)-C(21)	1.859(2)
Si(19)-C(22)	1.880(2)
C(22)-C(23)	1.527(3)
C(22)-C(24)	1.533(3)
C(22)-C(25)	1.535(3)
C(26)-C(27)	1.511(4)
C(28)-C(29)	1.509(3)
O(30)-C(31)	1.433(3)
C(32)-O(33)	1.142(3)
C(34)-O(35)	1.144(3)
C(36)-O(37)	1.142(3)
C(38)-O(39)	1.145(3)
C(40)-O(41)	1.152(3)
C(42)-O(43)	1.155(3)
C(34)-Mn(1)-C(36)	91.83(12)
C(34)-Mn(1)-C(32)	89.25(11)
C(36)-Mn(1)-C(32)	94.60(10)
C(34)-Mn(1)-C(3)	91.47(10)
C(36)-Mn(1)-C(3)	117.46(9)
C(32)-Mn(1)-C(3)	147.89(9)
C(34)-Mn(1)-C(2)	97.44(11)
C(36)-Mn(1)-C(2)	154.48(10)
C(32)-Mn(1)-C(2)	109.19(9)
C(3)-Mn(1)-C(2)	38.96(7)
C(34)-Mn(1)-C(1)	132.53(11)

C(36)-Mn(1)-C(1)	135.30(10)
C(32)-Mn(1)-C(1)	91.59(10)
C(3)-Mn(1)-C(1)	64.86(8)
C(2)-Mn(1)-C(1)	38.43(8)
C(34)-Mn(1)-C(17)	155.91(10)
C(36)-Mn(1)-C(17)	99.02(9)
C(32)-Mn(1)-C(17)	111.04(9)
C(3)-Mn(1)-C(17)	64.45(7)
C(2)-Mn(1)-C(17)	64.37(8)
C(1)-Mn(1)-C(17)	38.58(7)
C(34)-Mn(1)-C(12)	120.81(10)
C(36)-Mn(1)-C(12)	90.14(9)
C(32)-Mn(1)-C(12)	149.44(9)
C(3)-Mn(1)-C(12)	38.47(7)
C(2)-Mn(1)-C(12)	64.70(8)
C(1)-Mn(1)-C(12)	64.74(7)
C(17)-Mn(1)-C(12)	38.47(6)
C(40)-Cr(1)-C(42)	85.62(11)
C(40)-Cr(1)-C(38)	89.58(12)
C(42)-Cr(1)-C(38)	87.31(10)
C(40)-Cr(1)-C(8)	114.27(10)
C(42)-Cr(1)-C(8)	160.12(8)
C(38)-Cr(1)-C(8)	92.57(10)
C(40)-Cr(1)-C(9)	88.77(10)
C(42)-Cr(1)-C(9)	151.52(9)
C(38)-Cr(1)-C(9)	120.59(11)
C(8)-Cr(1)-C(9)	37.25(8)
C(40)-Cr(1)-C(11)	118.09(11)
C(42)-Cr(1)-C(11)	92.31(9)
C(38)-Cr(1)-C(11)	152.23(9)
C(8)-Cr(1)-C(11)	78.65(9)
C(9)-Cr(1)-C(11)	65.99(9)
C(40)-Cr(1)-C(10)	90.26(10)
C(42)-Cr(1)-C(10)	115.06(9)
C(38)-Cr(1)-C(10)	157.55(11)
C(8)-Cr(1)-C(10)	67.15(9)
C(9)-Cr(1)-C(10)	36.96(9)
C(11)-Cr(1)-C(10)	36.61(8)
C(40)-Cr(1)-C(16)	154.98(10)
C(42)-Cr(1)-C(16)	96.60(9)
C(38)-Cr(1)-C(16)	115.39(9)
C(8)-Cr(1)-C(16)	65.55(8)
C(9)-Cr(1)-C(16)	77.41(8)
C(11)-Cr(1)-C(16)	37.08(7)
C(10)-Cr(1)-C(16)	66.15(7)
C(40)-Cr(1)-C(15)	151.30(10)
C(42)-Cr(1)-C(15)	123.06(8)
C(38)-Cr(1)-C(15)	90.50(9)
C(8)-Cr(1)-C(15)	37.07(7)
C(9)-Cr(1)-C(15)	66.70(7)
C(11)-Cr(1)-C(15)	66.59(7)
C(10)-Cr(1)-C(15)	79.07(7)
C(16)-Cr(1)-C(15)	36.06(7)
C(2)-C(1)-C(17)	108.04(17)
C(2)-C(1)-Mn(1)	70.36(12)
C(17)-C(1)-Mn(1)	71.75(11)
C(1)-C(2)-C(3)	108.23(17)
C(1)-C(2)-Mn(1)	71.21(12)
C(3)-C(2)-Mn(1)	70.43(11)
C(12)-C(3)-C(2)	108.56(16)

C(12)-C(3)-Mn(1)	72.58(11)
C(2)-C(3)-Mn(1)	70.61(12)
O(18)-C(4)-C(5)	118.77(15)
O(18)-C(4)-C(13)	119.52(15)
C(5)-C(4)-C(13)	121.32(16)
C(4)-C(5)-C(6)	118.59(16)
C(4)-C(5)-C(26)	117.95(16)
C(6)-C(5)-C(26)	123.15(17)
C(5)-C(6)-C(7)	119.43(16)
C(5)-C(6)-C(28)	122.24(17)
C(7)-C(6)-C(28)	118.26(17)
O(30)-C(7)-C(6)	116.61(16)
O(30)-C(7)-C(14)	120.85(16)
C(6)-C(7)-C(14)	122.34(17)
C(9)-C(8)-C(15)	121.5(2)
C(9)-C(8)-Cr(1)	71.48(13)
C(15)-C(8)-Cr(1)	75.32(12)
C(10)-C(9)-C(8)	121.0(2)
C(10)-C(9)-Cr(1)	72.10(13)
C(8)-C(9)-Cr(1)	71.27(12)
C(11)-C(10)-C(9)	118.72(18)
C(11)-C(10)-Cr(1)	71.29(12)
C(9)-C(10)-Cr(1)	70.94(13)
C(10)-C(11)-C(16)	121.4(2)
C(10)-C(11)-Cr(1)	72.10(13)
C(16)-C(11)-Cr(1)	74.62(11)
C(3)-C(12)-C(17)	107.05(16)
C(3)-C(12)-C(13)	133.36(16)
C(17)-C(12)-C(13)	119.49(16)
C(3)-C(12)-Mn(1)	68.96(12)
C(17)-C(12)-Mn(1)	70.51(11)
C(13)-C(12)-Mn(1)	122.76(13)
C(4)-C(13)-C(14)	119.50(16)
C(4)-C(13)-C(12)	120.70(16)
C(14)-C(13)-C(12)	119.43(15)
C(7)-C(14)-C(13)	117.08(16)
C(7)-C(14)-C(15)	123.21(16)
C(13)-C(14)-C(15)	119.69(16)
C(16)-C(15)-C(8)	116.78(17)
C(16)-C(15)-C(14)	119.55(16)
C(8)-C(15)-C(14)	123.67(18)
C(16)-C(15)-Cr(1)	71.53(10)
C(8)-C(15)-Cr(1)	67.61(11)
C(14)-C(15)-Cr(1)	132.59(13)
C(15)-C(16)-C(11)	120.40(18)
C(15)-C(16)-C(17)	119.40(16)
C(11)-C(16)-C(17)	120.04(18)
C(15)-C(16)-Cr(1)	72.40(11)
C(11)-C(16)-Cr(1)	68.31(11)
C(17)-C(16)-Cr(1)	136.51(14)
C(1)-C(17)-C(12)	108.10(16)
C(1)-C(17)-C(16)	130.31(17)
C(12)-C(17)-C(16)	120.82(17)
C(1)-C(17)-Mn(1)	69.67(12)
C(12)-C(17)-Mn(1)	71.02(11)
C(16)-C(17)-Mn(1)	132.65(14)
C(4)-O(18)-Si(19)	125.95(12)
O(18)-Si(19)-C(20)	110.40(9)
O(18)-Si(19)-C(21)	111.47(10)
C(20)-Si(19)-C(21)	106.69(13)

O(18)-Si(19)-C(22)	103.20(9)
C(20)-Si(19)-C(22)	111.92(11)
C(21)-Si(19)-C(22)	113.24(11)
C(23)-C(22)-C(24)	109.3(2)
C(23)-C(22)-C(25)	108.3(2)
C(24)-C(22)-C(25)	108.7(2)
C(23)-C(22)-Si(19)	110.78(15)
C(24)-C(22)-Si(19)	109.89(17)
C(25)-C(22)-Si(19)	109.79(14)
C(27)-C(26)-C(5)	111.26(18)
C(29)-C(28)-C(6)	112.52(18)
C(7)-O(30)-C(31)	112.58(16)
O(33)-C(32)-Mn(1)	175.6(2)
O(35)-C(34)-Mn(1)	178.7(3)
O(37)-C(36)-Mn(1)	175.7(2)
O(39)-C(38)-Cr(1)	178.5(3)
O(41)-C(40)-Cr(1)	178.5(3)
O(43)-C(42)-Cr(1)	176.3(2)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **20**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Mn(1)	31(1)	23(1)	23(1)	4(1)	1(1)	3(1)
Cr(1)	22(1)	20(1)	37(1)	6(1)	1(1)	2(1)
C(1)	41(1)	31(1)	24(1)	5(1)	10(1)	7(1)
C(2)	50(1)	28(1)	22(1)	-2(1)	5(1)	8(1)
C(3)	39(1)	21(1)	24(1)	1(1)	3(1)	6(1)
C(4)	26(1)	17(1)	23(1)	2(1)	0(1)	3(1)
C(5)	27(1)	24(1)	22(1)	4(1)	2(1)	5(1)
C(6)	29(1)	25(1)	23(1)	1(1)	-1(1)	8(1)
C(7)	25(1)	19(1)	28(1)	-2(1)	-4(1)	6(1)
C(8)	27(1)	25(1)	45(1)	8(1)	-3(1)	1(1)
C(9)	20(1)	29(1)	63(2)	15(1)	0(1)	-1(1)
C(10)	26(1)	30(1)	55(1)	17(1)	13(1)	3(1)
C(11)	33(1)	29(1)	38(1)	12(1)	12(1)	7(1)
C(12)	29(1)	21(1)	21(1)	3(1)	5(1)	6(1)
C(13)	23(1)	19(1)	23(1)	2(1)	2(1)	5(1)
C(14)	22(1)	19(1)	28(1)	3(1)	1(1)	4(1)
C(15)	22(1)	21(1)	33(1)	6(1)	2(1)	5(1)
C(16)	25(1)	23(1)	33(1)	6(1)	9(1)	6(1)
C(17)	30(1)	23(1)	25(1)	5(1)	7(1)	7(1)
O(18)	28(1)	17(1)	25(1)	2(1)	1(1)	2(1)
Si(19)	26(1)	20(1)	27(1)	3(1)	3(1)	3(1)
C(20)	42(1)	40(1)	55(1)	11(1)	21(1)	16(1)
C(21)	47(1)	44(1)	45(1)	7(1)	-12(1)	14(1)
C(22)	34(1)	22(1)	33(1)	2(1)	5(1)	-1(1)
C(23)	49(2)	57(2)	47(1)	-2(1)	16(1)	-21(1)
C(24)	68(2)	22(1)	83(2)	3(1)	-2(2)	3(1)
C(25)	46(1)	42(1)	44(1)	3(1)	-9(1)	-8(1)
C(26)	43(1)	31(1)	24(1)	5(1)	8(1)	1(1)
C(27)	38(1)	50(1)	65(2)	11(1)	15(1)	2(1)
C(28)	38(1)	33(1)	23(1)	-2(1)	-1(1)	8(1)

C(29)	57(2)	56(2)	41(1)	-13(1)	-1(1)	28(1)
O(30)	29(1)	23(1)	36(1)	-5(1)	-7(1)	3(1)
C(31)	31(1)	44(1)	40(1)	0(1)	-10(1)	5(1)
C(32)	42(1)	29(1)	32(1)	3(1)	-2(1)	3(1)
O(33)	69(1)	46(1)	44(1)	15(1)	-9(1)	17(1)
C(34)	42(1)	35(1)	57(2)	10(1)	0(1)	0(1)
O(35)	48(1)	57(1)	127(2)	15(1)	-3(1)	-18(1)
C(36)	36(1)	48(1)	36(1)	1(1)	-2(1)	21(1)
O(37)	66(1)	95(2)	41(1)	-12(1)	2(1)	50(1)
C(38)	40(1)	38(1)	39(1)	-3(1)	-1(1)	9(1)
O(39)	67(1)	84(2)	52(1)	-14(1)	18(1)	19(1)
C(40)	27(1)	28(1)	85(2)	12(1)	-2(1)	3(1)
O(41)	51(1)	25(1)	162(3)	18(1)	-5(1)	1(1)
C(42)	30(1)	30(1)	39(1)	8(1)	4(1)	5(1)
O(43)	38(1)	64(1)	56(1)	17(1)	-9(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **20**.

	x	y	z	U(eq)
H(1)	4361	7538	-226	38
H(2)	2728	5879	-280	40
H(3)	2485	5464	1244	34
H(8)	7743	9472	3322	39
H(9)	9383	10399	2388	45
H(10)	8687	10151	902	44
H(11)	6370	8939	360	39
H(20A)	4487	4353	1334	66
H(20B)	5708	3873	1947	66
H(20C)	5997	4982	1974	66
H(21A)	5374	4998	3967	67
H(21B)	5318	3903	3716	67
H(21C)	3687	4281	4222	67
H(23A)	-1035	3060	3115	81
H(23B)	-465	4165	3308	81
H(23C)	629	3486	3770	81
H(24A)	839	2102	2203	87
H(24B)	2513	2449	2873	87
H(24C)	2751	2565	1882	87
H(25A)	1107	3727	1205	69
H(25B)	-154	4324	1777	69
H(25C)	-755	3225	1544	69
H(26A)	1780	5368	4309	39
H(26B)	1874	6191	5078	39
H(27A)	-386	6833	4371	76
H(27B)	-1141	5774	4488	76
H(27C)	-448	6039	3581	76
H(28A)	3464	7320	5634	38
H(28B)	5074	8161	5559	38
H(29A)	2936	9076	5115	76
H(29B)	2439	8751	6029	76
H(29C)	1324	8235	5187	76
H(31A)	7728	8214	5026	59
H(31B)	8562	9278	4969	59

H(31C)	8698	8506	4180	59

2.9 Tricarbonyl-{pentacarbonyl[8-benzo[*e*]indenyl-(methoxy)carbene]chromium[ŋ^5-1,2,3,3a,9a]}rhenium (23)

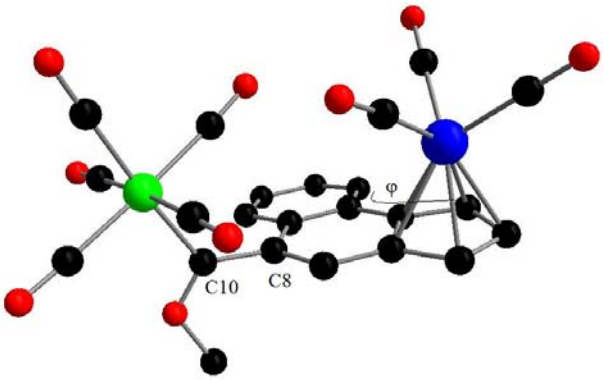


Table 1. Crystal data and structure refinement for **23**.

Empirical formula	C23 H11 Cr O9 Re
Formula weight	669.52
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 6.6632(2) A alpha = 86.9302(13) deg.
	b = 7.6117(2) A beta = 83.6408(16) deg.
	c = 21.2929(6) A gamma = 89.4973(16) deg.
Volume	1071.75(5) A^3
Z, Calculated density	2, 2.075 Mg/m^3
Absorption coefficient	6.204 mm^-1
F(000)	640
Crystal size	0.64 x 0.20 x 0.16 mm
Theta range for data collection	2.68 to 29.99 deg.
Limiting indices	-9<=h<=9, -10<=k<=10, -29<=l<=29
Reflections collected / unique	12551 / 5912 [R(int) = 0.0553]
Completeness to theta = 29.99	94.5 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.32403 and 0.13039
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5912 / 0 / 329
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0520
R indices (all data)	R1 = 0.0274, wR2 = 0.0527
Extinction coefficient	0.0024(3)
Largest diff. peak and hole	1.739 and -1.719 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **23**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6142(4)	-2930(3)	818(1)	22(1)
C(2)	8091(4)	-2182(3)	824(1)	22(1)
C(3)	8337(4)	-1802(4)	1458(1)	20(1)
C(3A)	6568(4)	-2384(3)	1854(1)	18(1)
C(4)	6028(4)	-2358(4)	2521(1)	21(1)
C(5)	4231(4)	-3035(3)	2790(1)	20(1)
C(5A)	2866(4)	-3875(3)	2406(1)	19(1)
C(6)	1084(4)	-4717(3)	2692(2)	23(1)
C(7)	-129(4)	-5611(4)	2334(2)	27(1)
C(8)	374(4)	-5676(4)	1679(2)	28(1)
C(9)	2071(4)	-4831(3)	1383(2)	23(1)
C(9A)	3337(4)	-3911(3)	1744(1)	19(1)
C(9B)	5203(4)	-3095(3)	1459(1)	19(1)
C(10)	3621(4)	-2834(5)	3477(2)	30(1)
C(11)	5194(10)	-5435(8)	3697(3)	28(1)

C(11S)	3964(11)	-4960(9)	4399(3)	29(2)
C(12)	1081(6)	1553(5)	4036(2)	44(1)
C(13)	2993(5)	-1097(4)	4628(2)	31(1)
C(14)	4850(5)	467(5)	3576(2)	42(1)
C(15)	1449(4)	-120(4)	2973(2)	28(1)
C(16)	-181(5)	-1854(4)	4051(2)	33(1)
C(17)	5357(4)	1556(3)	1784(1)	22(1)
C(18)	6893(4)	1731(3)	572(1)	20(1)
C(19)	3157(4)	494(3)	864(1)	20(1)
Cr	2276(1)	-632(1)	3797(1)	30(1)
O(1)	4064(7)	-3876(7)	3892(2)	24(1)
O(1S)	4218(9)	-4604(8)	3724(3)	23(1)
O(2)	386(5)	2871(4)	4171(2)	63(1)
O(3)	3383(4)	-1335(3)	5130(1)	42(1)
O(4)	6410(3)	1043(4)	3453(1)	52(1)
O(5)	883(3)	231(3)	2501(1)	34(1)
O(6)	-1628(3)	-2612(4)	4207(1)	47(1)
O(7)	5192(3)	2492(3)	2198(1)	30(1)
O(8)	7601(3)	2837(3)	227(1)	29(1)
O(9)	1611(3)	833(3)	692(1)	27(1)
Re	5736(1)	-98(1)	1139(1)	15(1)

Table 3. Bond lengths [A] and angles [deg] for **23**.

C(1)-C(2)	1.424(3)
C(1)-C(9B)	1.437(4)
C(1)-Re	2.301(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.424(4)

C(2)-Re	2.295(3)
C(2)-H(2A)	0.9500
C(3)-C(3A)	1.431(4)
C(3)-Re	2.297(2)
C(3)-H(3A)	0.9500
C(3A)-C(4)	1.427(4)
C(3A)-C(9B)	1.434(3)
C(3A)-Re	2.354(2)
C(4)-C(5)	1.361(3)
C(4)-H(4A)	0.9500
C(5)-C(5A)	1.462(4)
C(5)-C(10)	1.489(4)
C(5A)-C(9A)	1.410(4)
C(5A)-C(6)	1.415(3)
C(6)-C(7)	1.378(4)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.401(4)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.378(4)
C(8)-H(8A)	0.9500
C(9)-C(9A)	1.416(4)
C(9)-H(9A)	0.9500
C(9A)-C(9B)	1.452(4)
C(9B)-Re	2.364(2)
C(10)-O(1)	1.216(5)
C(10)-O(1S)	1.488(6)
C(10)-Cr	2.009(4)
C(11)-O(1)	1.454(9)
C(11)-H(11C)	0.9800
C(11)-H(11B)	0.9800

C(11)-H(11A)	0.9800
C(11S)-O(1S)	1.440(8)
C(11S)-H(11F)	0.9800
C(11S)-H(11E)	0.9800
C(11S)-H(11D)	0.9800
C(12)-O(2)	1.139(5)
C(12)-Cr	1.907(5)
C(13)-O(3)	1.131(4)
C(13)-Cr	1.900(3)
C(14)-O(4)	1.130(3)
C(14)-Cr	1.915(3)
C(15)-O(5)	1.132(3)
C(15)-Cr	1.914(3)
C(16)-O(6)	1.137(3)
C(16)-Cr	1.901(3)
C(17)-O(7)	1.159(4)
C(17)-Re	1.908(3)
C(18)-O(8)	1.155(3)
C(18)-Re	1.904(3)
C(19)-O(9)	1.154(3)
C(19)-Re	1.918(2)
C(2)-C(1)-C(9B)	108.0(2)
C(2)-C(1)-Re	71.71(15)
C(9B)-C(1)-Re	74.47(16)
C(2)-C(1)-H(1A)	126.0
C(9B)-C(1)-H(1A)	126.0
Re-C(1)-H(1A)	119.7
C(3)-C(2)-C(1)	108.3(2)
C(3)-C(2)-Re	72.01(16)
C(1)-C(2)-Re	72.18(16)

C(3)-C(2)-H(2A)	125.9
C(1)-C(2)-H(2A)	125.9
Re-C(2)-H(2A)	121.6
C(2)-C(3)-C(3A)	108.1(2)
C(2)-C(3)-Re	71.86(14)
C(3A)-C(3)-Re	74.27(14)
C(2)-C(3)-H(3A)	125.9
C(3A)-C(3)-H(3A)	125.9
Re-C(3)-H(3A)	119.8
C(4)-C(3A)-C(3)	131.9(2)
C(4)-C(3A)-C(9B)	120.2(2)
C(3)-C(3A)-C(9B)	107.9(2)
C(4)-C(3A)-Re	123.02(19)
C(3)-C(3A)-Re	69.91(14)
C(9B)-C(3A)-Re	72.68(14)
C(5)-C(4)-C(3A)	120.4(2)
C(5)-C(4)-H(4A)	119.8
C(3A)-C(4)-H(4A)	119.8
C(4)-C(5)-C(5A)	120.7(3)
C(4)-C(5)-C(10)	119.2(2)
C(5A)-C(5)-C(10)	120.1(2)
C(9A)-C(5A)-C(6)	118.8(2)
C(9A)-C(5A)-C(5)	120.5(2)
C(6)-C(5A)-C(5)	120.7(3)
C(7)-C(6)-C(5A)	120.6(3)
C(7)-C(6)-H(6A)	119.7
C(5A)-C(6)-H(6A)	119.7
C(6)-C(7)-C(8)	120.3(3)
C(6)-C(7)-H(7A)	119.9
C(8)-C(7)-H(7A)	119.9

C(9)-C(8)-C(7) 120.6(3)

C(9)-C(8)-H(8A) 119.7

C(7)-C(8)-H(8A) 119.7

C(8)-C(9)-C(9A) 119.9(3)

C(8)-C(9)-H(9A) 120.1

C(9A)-C(9)-H(9A) 120.1

C(5A)-C(9A)-C(9) 119.8(2)

C(5A)-C(9A)-C(9B) 118.3(2)

C(9)-C(9A)-C(9B) 121.7(3)

C(3A)-C(9B)-C(1) 107.6(2)

C(3A)-C(9B)-C(9A) 119.7(2)

C(1)-C(9B)-C(9A) 132.6(2)

C(3A)-C(9B)-Re 71.93(14)

C(1)-C(9B)-Re 69.68(14)

C(9A)-C(9B)-Re 127.43(18)

O(1)-C(10)-O(1S) 26.7(3)

O(1)-C(10)-C(5) 123.9(4)

O(1S)-C(10)-C(5) 99.0(4)

O(1)-C(10)-Cr 114.0(4)

O(1S)-C(10)-Cr 139.2(3)

C(5)-C(10)-Cr 121.7(2)

O(1S)-C(11S)-H(11F) 109.5

O(1S)-C(11S)-H(11E) 109.5

H(11F)-C(11S)-H(11E) 109.5

O(1S)-C(11S)-H(11D) 109.5

H(11F)-C(11S)-H(11D) 109.5

H(11E)-C(11S)-H(11D) 109.5

O(2)-C(12)-Cr 178.9(3)

O(3)-C(13)-Cr 178.0(3)

O(4)-C(14)-Cr 176.8(4)

O(5)-C(15)-Cr	176.6(3)
O(6)-C(16)-Cr	178.6(3)
O(7)-C(17)-Re	175.9(2)
O(8)-C(18)-Re	179.7(3)
O(9)-C(19)-Re	179.0(3)
C(13)-Cr-C(16)	88.13(13)
C(13)-Cr-C(12)	90.60(15)
C(16)-Cr-C(12)	91.62(15)
C(13)-Cr-C(15)	177.58(15)
C(16)-Cr-C(15)	90.44(13)
C(12)-Cr-C(15)	87.49(15)
C(13)-Cr-C(14)	88.59(12)
C(16)-Cr-C(14)	175.71(16)
C(12)-Cr-C(14)	91.18(17)
C(15)-Cr-C(14)	92.93(12)
C(13)-Cr-C(10)	93.01(14)
C(16)-Cr-C(10)	91.47(13)
C(12)-Cr-C(10)	175.33(13)
C(15)-Cr-C(10)	88.97(13)
C(14)-Cr-C(10)	85.95(16)
C(10)-O(1)-C(11)	117.2(5)
C(11S)-O(1S)-C(10)	117.8(6)
C(18)-Re-C(17)	88.80(11)
C(18)-Re-C(19)	88.45(10)
C(17)-Re-C(19)	91.13(11)
C(18)-Re-C(2)	95.19(11)
C(17)-Re-C(2)	136.98(10)
C(19)-Re-C(2)	131.70(11)
C(18)-Re-C(3)	107.55(10)
C(17)-Re-C(3)	102.14(10)

C(19)-Re-C(3)	159.20(10)
C(2)-Re-C(3)	36.13(10)
C(18)-Re-C(1)	116.93(11)
C(17)-Re-C(1)	151.55(10)
C(19)-Re-C(1)	100.94(10)
C(2)-Re-C(1)	36.11(9)
C(3)-Re-C(1)	60.26(9)
C(18)-Re-C(3A)	142.58(9)
C(17)-Re-C(3A)	92.71(10)
C(19)-Re-C(3A)	128.86(9)
C(2)-Re-C(3A)	59.62(10)
C(3)-Re-C(3A)	35.81(9)
C(1)-Re-C(3A)	59.67(10)
C(18)-Re-C(9B)	152.41(12)
C(17)-Re-C(9B)	116.91(10)
C(19)-Re-C(9B)	100.18(9)
C(2)-Re-C(9B)	59.58(10)
C(3)-Re-C(9B)	59.58(9)
C(1)-Re-C(9B)	35.85(9)
C(3A)-Re-C(9B)	35.39(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **23**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	24(1)	23(1)	20(2)	-1(1)	-3(1)	7(1)

C(2)	20(1)	24(1)	20(1)	0(1)	4(1)	10(1)
C(3)	14(1)	28(1)	18(1)	1(1)	0(1)	5(1)
C(3A)	15(1)	22(1)	17(1)	2(1)	-1(1)	5(1)
C(4)	15(1)	32(1)	17(1)	0(1)	-3(1)	3(1)
C(5)	17(1)	27(1)	16(1)	4(1)	-2(1)	4(1)
C(5A)	20(1)	18(1)	20(1)	2(1)	-2(1)	3(1)
C(6)	24(1)	19(1)	24(2)	4(1)	0(1)	1(1)
C(7)	23(1)	21(1)	37(2)	1(1)	-1(1)	-2(1)
C(8)	28(1)	20(1)	36(2)	-6(1)	-6(1)	-2(1)
C(9)	28(1)	18(1)	24(2)	-3(1)	-5(1)	3(1)
C(9A)	20(1)	14(1)	22(2)	1(1)	-2(1)	4(1)
C(9B)	21(1)	17(1)	19(1)	-1(1)	-2(1)	5(1)
C(10)	13(1)	58(2)	20(2)	4(1)	-5(1)	-9(1)
C(11)	35(3)	26(3)	23(3)	2(2)	-2(2)	5(2)
C(11S)	39(4)	31(3)	16(4)	9(3)	-3(3)	-3(3)
C(12)	45(2)	53(2)	30(2)	-11(2)	12(2)	-30(2)
C(13)	30(2)	38(2)	22(2)	-6(1)	6(1)	-15(1)
C(14)	37(2)	78(3)	12(2)	-4(2)	-2(1)	-25(2)
C(15)	20(1)	37(2)	28(2)	-13(1)	2(1)	-5(1)
C(16)	26(2)	41(2)	33(2)	-13(1)	3(1)	-6(1)
C(17)	21(1)	22(1)	22(2)	5(1)	-6(1)	2(1)
C(18)	17(1)	23(1)	21(2)	-2(1)	-3(1)	3(1)
C(19)	19(1)	21(1)	19(1)	1(1)	0(1)	0(1)
Cr	22(1)	52(1)	17(1)	-10(1)	4(1)	-15(1)
O(1)	28(2)	23(2)	21(3)	0(2)	0(2)	4(2)
O(1S)	26(3)	18(3)	26(3)	4(2)	-6(2)	3(3)
O(2)	88(2)	45(2)	51(2)	-16(1)	28(2)	-25(2)
O(3)	48(1)	55(2)	22(1)	2(1)	-4(1)	-15(1)
O(4)	31(1)	98(2)	26(1)	5(1)	-3(1)	-33(1)
O(5)	36(1)	33(1)	34(1)	-8(1)	-11(1)	5(1)

O(6)	28(1)	50(2)	61(2)	-6(1)	5(1)	-15(1)
O(7)	39(1)	26(1)	27(1)	-9(1)	-9(1)	7(1)
O(8)	27(1)	31(1)	27(1)	6(1)	1(1)	-5(1)
O(9)	16(1)	37(1)	29(1)	1(1)	-5(1)	2(1)
Re	14(1)	18(1)	14(1)	-1(1)	-1(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **23**.

	x	y	z	U(eq)
H(1A)	5563	-3261	453	26
H(2A)	9060	-1973	466	26
H(3A)	9479	-1257	1594	24
H(4A)	6928	-1865	2780	25
H(6A)	720	-4665	3135	28
H(7A)	-1312	-6185	2532	32
H(8A)	-461	-6308	1437	33
H(9A)	2390	-4866	938	28
H(11C)	5258	-6260	4063	42
H(11B)	6566	-5096	3521	42
H(11A)	4519	-5998	3374	42
H(11F)	4116	-6225	4494	43
H(11E)	2615	-4579	4572	43
H(11D)	4987	-4318	4591	43

Table 6. Torsion angles [deg] for **23**.

C(9B)-C(1)-C(2)-C(3)	-2.7(3)

Re-C(1)-C(2)-C(3)	63.40(19)
C(9B)-C(1)-C(2)-Re	-66.15(18)
C(1)-C(2)-C(3)-C(3A)	2.4(3)
Re-C(2)-C(3)-C(3A)	65.95(18)
C(1)-C(2)-C(3)-Re	-63.52(18)
C(2)-C(3)-C(3A)-C(4)	178.8(3)
Re-C(3)-C(3A)-C(4)	-116.8(3)
C(2)-C(3)-C(3A)-C(9B)	-1.2(3)
Re-C(3)-C(3A)-C(9B)	63.18(18)
C(2)-C(3)-C(3A)-Re	-64.36(18)
C(3)-C(3A)-C(4)-C(5)	-178.8(3)
C(9B)-C(3A)-C(4)-C(5)	1.2(4)
Re-C(3A)-C(4)-C(5)	89.3(3)
C(3A)-C(4)-C(5)-C(5A)	3.0(4)
C(3A)-C(4)-C(5)-C(10)	-174.1(3)
C(4)-C(5)-C(5A)-C(9A)	-3.6(4)
C(10)-C(5)-C(5A)-C(9A)	173.5(3)
C(4)-C(5)-C(5A)-C(6)	174.3(3)
C(10)-C(5)-C(5A)-C(6)	-8.6(4)
C(9A)-C(5A)-C(6)-C(7)	2.3(4)
C(5)-C(5A)-C(6)-C(7)	-175.6(3)
C(5A)-C(6)-C(7)-C(8)	-0.9(4)
C(6)-C(7)-C(8)-C(9)	-0.8(4)
C(7)-C(8)-C(9)-C(9A)	1.0(4)
C(6)-C(5A)-C(9A)-C(9)	-2.1(4)
C(5)-C(5A)-C(9A)-C(9)	175.8(2)
C(6)-C(5A)-C(9A)-C(9B)	-177.9(2)
C(5)-C(5A)-C(9A)-C(9B)	0.0(4)
C(8)-C(9)-C(9A)-C(5A)	0.5(4)
C(8)-C(9)-C(9A)-C(9B)	176.2(2)

C(4)-C(3A)-C(9B)-C(1)	179.5(2)
C(3)-C(3A)-C(9B)-C(1)	-0.5(3)
Re-C(3A)-C(9B)-C(1)	60.89(17)
C(4)-C(3A)-C(9B)-C(9A)	-4.7(4)
C(3)-C(3A)-C(9B)-C(9A)	175.2(2)
Re-C(3A)-C(9B)-C(9A)	-123.4(2)
C(4)-C(3A)-C(9B)-Re	118.6(2)
C(3)-C(3A)-C(9B)-Re	-61.39(18)
C(2)-C(1)-C(9B)-C(3A)	2.0(3)
Re-C(1)-C(9B)-C(3A)	-62.34(18)
C(2)-C(1)-C(9B)-C(9A)	-173.0(3)
Re-C(1)-C(9B)-C(9A)	122.7(3)
C(2)-C(1)-C(9B)-Re	64.34(18)
C(5A)-C(9A)-C(9B)-C(3A)	4.1(4)
C(9)-C(9A)-C(9B)-C(3A)	-171.7(2)
C(5A)-C(9A)-C(9B)-C(1)	178.6(3)
C(9)-C(9A)-C(9B)-C(1)	2.8(4)
C(5A)-C(9A)-C(9B)-Re	-85.2(3)
C(9)-C(9A)-C(9B)-Re	99.1(3)
C(4)-C(5)-C(10)-O(1)	-88.6(4)
C(5A)-C(5)-C(10)-O(1)	94.3(4)
C(4)-C(5)-C(10)-O(1S)	-99.1(3)
C(5A)-C(5)-C(10)-O(1S)	83.8(3)
C(4)-C(5)-C(10)-Cr	83.5(3)
C(5A)-C(5)-C(10)-Cr	-93.6(3)
O(3)-C(13)-Cr-C(16)	-79(7)
O(3)-C(13)-Cr-C(12)	13(7)
O(3)-C(13)-Cr-C(15)	-25(9)
O(3)-C(13)-Cr-C(14)	104(7)
O(3)-C(13)-Cr-C(10)	-170(7)

O(6)-C(16)-Cr-C(13)	-55(14)
O(6)-C(16)-Cr-C(12)	-146(14)
O(6)-C(16)-Cr-C(15)	127(14)
O(6)-C(16)-Cr-C(14)	-15(16)
O(6)-C(16)-Cr-C(10)	38(14)
O(2)-C(12)-Cr-C(13)	127(21)
O(2)-C(12)-Cr-C(16)	-145(21)
O(2)-C(12)-Cr-C(15)	-55(21)
O(2)-C(12)-Cr-C(14)	38(21)
O(2)-C(12)-Cr-C(10)	-14(22)
O(5)-C(15)-Cr-C(13)	10(6)
O(5)-C(15)-Cr-C(16)	64(4)
O(5)-C(15)-Cr-C(12)	-27(4)
O(5)-C(15)-Cr-C(14)	-118(4)
O(5)-C(15)-Cr-C(10)	156(4)
O(4)-C(14)-Cr-C(13)	60(6)
O(4)-C(14)-Cr-C(16)	20(7)
O(4)-C(14)-Cr-C(12)	150(6)
O(4)-C(14)-Cr-C(15)	-122(6)
O(4)-C(14)-Cr-C(10)	-33(6)
O(1)-C(10)-Cr-C(13)	13.5(3)
O(1S)-C(10)-Cr-C(13)	24.7(4)
C(5)-C(10)-Cr-C(13)	-159.3(2)
O(1)-C(10)-Cr-C(16)	-74.7(3)
O(1S)-C(10)-Cr-C(16)	-63.6(4)
C(5)-C(10)-Cr-C(16)	112.5(2)
O(1)-C(10)-Cr-C(12)	154.1(14)
O(1S)-C(10)-Cr-C(12)	165.2(14)
C(5)-C(10)-Cr-C(12)	-18.8(16)
O(1)-C(10)-Cr-C(15)	-165.1(3)

O(1S)-C(10)-Cr-C(15)	-154.0(4)
C(5)-C(10)-Cr-C(15)	22.0(2)
O(1)-C(10)-Cr-C(14)	101.9(3)
O(1S)-C(10)-Cr-C(14)	113.0(4)
C(5)-C(10)-Cr-C(14)	-71.0(2)
O(1S)-C(10)-O(1)-C(11)	21.3(7)
C(5)-C(10)-O(1)-C(11)	-2.3(6)
Cr-C(10)-O(1)-C(11)	-175.0(3)
O(1)-C(10)-O(1S)-C(11S)	16.9(6)
C(5)-C(10)-O(1S)-C(11S)	177.2(5)
Cr-C(10)-O(1S)-C(11S)	-6.2(7)
O(8)-C(18)-Re-C(17)	129(55)
O(8)-C(18)-Re-C(19)	-140(100)
O(8)-C(18)-Re-C(2)	-8(55)
O(8)-C(18)-Re-C(3)	27(55)
O(8)-C(18)-Re-C(1)	-38(55)
O(8)-C(18)-Re-C(3A)	36(55)
O(8)-C(18)-Re-C(9B)	-30(55)
O(7)-C(17)-Re-C(18)	-125(3)
O(7)-C(17)-Re-C(19)	147(3)
O(7)-C(17)-Re-C(2)	-28(3)
O(7)-C(17)-Re-C(3)	-17(3)
O(7)-C(17)-Re-C(1)	31(3)
O(7)-C(17)-Re-C(3A)	18(3)
O(7)-C(17)-Re-C(9B)	45(3)
O(9)-C(19)-Re-C(18)	88(14)
O(9)-C(19)-Re-C(17)	176(100)
O(9)-C(19)-Re-C(2)	-8(14)
O(9)-C(19)-Re-C(3)	-54(14)
O(9)-C(19)-Re-C(1)	-30(14)

O(9)-C(19)-Re-C(3A)	-89(14)
O(9)-C(19)-Re-C(9B)	-66(14)
C(3)-C(2)-Re-C(18)	112.89(16)
C(1)-C(2)-Re-C(18)	-130.34(16)
C(3)-C(2)-Re-C(17)	19.1(2)
C(1)-C(2)-Re-C(17)	135.86(17)
C(3)-C(2)-Re-C(19)	-154.56(16)
C(1)-C(2)-Re-C(19)	-37.8(2)
C(1)-C(2)-Re-C(3)	116.8(2)
C(3)-C(2)-Re-C(1)	-116.8(2)
C(3)-C(2)-Re-C(3A)	-37.69(14)
C(1)-C(2)-Re-C(3A)	79.07(16)
C(3)-C(2)-Re-C(9B)	-78.96(16)
C(1)-C(2)-Re-C(9B)	37.81(14)
C(2)-C(3)-Re-C(18)	-74.20(17)
C(3A)-C(3)-Re-C(18)	170.16(16)
C(2)-C(3)-Re-C(17)	-166.81(15)
C(3A)-C(3)-Re-C(17)	77.55(18)
C(2)-C(3)-Re-C(19)	64.6(4)
C(3A)-C(3)-Re-C(19)	-51.0(4)
C(3A)-C(3)-Re-C(2)	-115.6(2)
C(2)-C(3)-Re-C(1)	37.30(15)
C(3A)-C(3)-Re-C(1)	-78.34(17)
C(2)-C(3)-Re-C(3A)	115.6(2)
C(2)-C(3)-Re-C(9B)	78.96(16)
C(3A)-C(3)-Re-C(9B)	-36.68(16)
C(2)-C(1)-Re-C(18)	58.37(18)
C(9B)-C(1)-Re-C(18)	173.87(13)
C(2)-C(1)-Re-C(17)	-94.3(2)
C(9B)-C(1)-Re-C(17)	21.2(3)

C(2)-C(1)-Re-C(19)	152.23(16)
C(9B)-C(1)-Re-C(19)	-92.28(15)
C(9B)-C(1)-Re-C(2)	115.5(2)
C(2)-C(1)-Re-C(3)	-37.32(15)
C(9B)-C(1)-Re-C(3)	78.17(15)
C(2)-C(1)-Re-C(3A)	-78.92(16)
C(9B)-C(1)-Re-C(3A)	36.58(13)
C(2)-C(1)-Re-C(9B)	-115.5(2)
C(4)-C(3A)-Re-C(18)	112.0(2)
C(3)-C(3A)-Re-C(18)	-15.6(3)
C(9B)-C(3A)-Re-C(18)	-132.7(2)
C(4)-C(3A)-Re-C(17)	20.5(2)
C(3)-C(3A)-Re-C(17)	-107.11(17)
C(9B)-C(3A)-Re-C(17)	135.70(18)
C(4)-C(3A)-Re-C(19)	-73.2(2)
C(3)-C(3A)-Re-C(19)	159.24(17)
C(9B)-C(3A)-Re-C(19)	42.1(2)
C(4)-C(3A)-Re-C(2)	165.6(2)
C(3)-C(3A)-Re-C(2)	38.04(16)
C(9B)-C(3A)-Re-C(2)	-79.15(18)
C(4)-C(3A)-Re-C(3)	127.6(3)
C(9B)-C(3A)-Re-C(3)	-117.2(2)
C(4)-C(3A)-Re-C(1)	-152.3(2)
C(3)-C(3A)-Re-C(1)	80.13(18)
C(9B)-C(3A)-Re-C(1)	-37.06(16)
C(4)-C(3A)-Re-C(9B)	-115.2(3)
C(3)-C(3A)-Re-C(9B)	117.2(2)
C(3A)-C(9B)-Re-C(18)	105.5(2)
C(1)-C(9B)-Re-C(18)	-11.9(3)
C(9A)-C(9B)-Re-C(18)	-140.5(2)

C(3A)-C(9B)-Re-C(17)	-51.48(19)
C(1)-C(9B)-Re-C(17)	-168.84(14)
C(9A)-C(9B)-Re-C(17)	62.5(3)
C(3A)-C(9B)-Re-C(19)	-148.00(18)
C(1)-C(9B)-Re-C(19)	94.64(16)
C(9A)-C(9B)-Re-C(19)	-34.0(3)
C(3A)-C(9B)-Re-C(2)	79.28(17)
C(1)-C(9B)-Re-C(2)	-38.08(14)
C(9A)-C(9B)-Re-C(2)	-166.8(3)
C(3A)-C(9B)-Re-C(3)	37.12(16)
C(1)-C(9B)-Re-C(3)	-80.24(16)
C(9A)-C(9B)-Re-C(3)	151.1(3)
C(3A)-C(9B)-Re-C(1)	117.4(2)
C(9A)-C(9B)-Re-C(1)	-128.7(3)
C(1)-C(9B)-Re-C(3A)	-117.4(2)
C(9A)-C(9B)-Re-C(3A)	114.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **23** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.10 *Anti*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}rhenium (24)

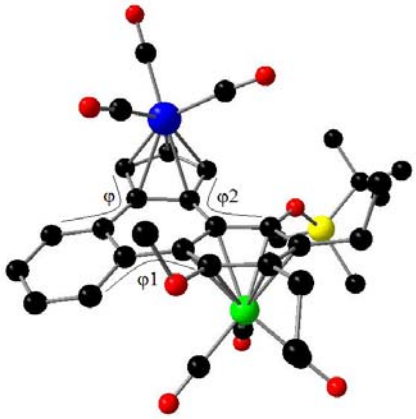


Table 1. Crystal data and structure refinement for**24**.

Empirical formula	C35 H37 Cl2 Cr O8 Re Si
Formula weight	922.84
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 14.6363(4) A alpha = 90 deg.
	b = 14.0920(4) A beta = 112.4210(10) deg.
	c = 19.1872(5) A gamma = 90 deg.
Volume	3658.29(17) A^3
Z, Calculated density	4, 1.676 Mg/m^3
Absorption coefficient	3.830 mm^-1
F(000)	1832
Crystal size	0.50 x 0.48 x 0.20 mm
Theta range for data collection	1.85 to 25.00 deg.
Limiting indices	-14<=h<=17, -16<=k<=16, -22<=l<=14
Reflections collected / unique	16451 / 6147 [R(int) = 0.0440]
Completeness to theta = 25.00	95.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.42435 and 0.24121
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6147 / 0 / 433
Goodness-of-fit on F^2	1.193

Final R indices [I>2sigma(I)] R1 = 0.0259, wR2 = 0.0765

R indices (all data) R1 = 0.0328, wR2 = 0.0943

Largest diff. peak and hole 0.970 and -1.882 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **24**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	1202(3)	6942(3)	1223(3)	22(1)
C(2)	1332(3)	7183(3)	1982(3)	25(1)
C(3)	1666(3)	6377(3)	2444(3)	21(1)
C(3A)	1741(3)	5603(3)	1979(2)	16(1)
C(3B)	2149(3)	4635(3)	2157(2)	15(1)
C(4)	2494(3)	4255(3)	2902(2)	16(1)
C(5)	3086(3)	3423(3)	3086(3)	17(1)
C(6)	3332(3)	2968(3)	2515(3)	19(1)
C(7)	2951(3)	3327(3)	1776(3)	18(1)
C(7A)	2292(3)	4118(3)	1563(2)	15(1)
C(7B)	1792(3)	4427(3)	766(2)	17(1)
C(8)	1640(3)	3812(3)	158(3)	21(1)
C(9)	1145(3)	4108(4)	-578(3)	24(1)
C(10)	801(3)	5033(4)	-732(3)	24(1)
C(11)	926(3)	5651(3)	-147(3)	22(1)
C(11A)	1406(3)	5356(3)	602(2)	17(1)
C(11B)	1446(3)	5960(3)	1225(2)	17(1)
C(12)	1249(3)	3472(4)	4078(3)	26(1)
C(13)	370(3)	5312(4)	3316(3)	28(1)
C(14)	2191(3)	5358(4)	4807(3)	25(1)

C(15)	1507(4)	5380(4)	5252(3)	34(1)
C(16)	3160(4)	4841(4)	5288(3)	35(1)
C(17)	2435(4)	6375(4)	4659(3)	41(1)
C(18)	3553(4)	3106(3)	3900(3)	23(1)
C(19)	4590(3)	3536(4)	4274(3)	32(1)
C(20)	4048(3)	2141(3)	2685(3)	25(1)
C(21)	3624(4)	1199(3)	2315(3)	33(1)
C(22)	3982(4)	3415(4)	1089(3)	34(1)
C(23)	3940(4)	6426(4)	2897(3)	28(1)
C(24)	3557(3)	6403(4)	1368(3)	30(1)
C(25)	3387(4)	8027(4)	2060(3)	34(1)
C(26)	1026(3)	2410(3)	1241(3)	23(1)
C(27)	1651(3)	1949(3)	2631(3)	21(1)
C(28)	444(4)	3280(3)	2113(3)	23(1)
C(29)	-3043(6)	4514(5)	957(6)	80(3)
Cl(1)	-3306(2)	3373(1)	1104(2)	94(1)
Cl(2)	-3987(2)	5297(1)	809(1)	87(1)
Cr	1676(1)	3049(1)	2126(1)	15(1)
O(1)	2342(2)	4755(2)	3456(2)	18(1)
O(2)	3242(2)	2879(2)	1255(2)	24(1)
O(3)	4549(3)	6200(3)	3461(2)	43(1)
O(4)	3922(3)	6144(3)	969(2)	49(1)
O(5)	3702(3)	8784(3)	2102(2)	54(1)
O(6)	590(3)	2018(3)	681(2)	36(1)
O(7)	1633(2)	1265(2)	2956(2)	31(1)
O(8)	-357(3)	3379(3)	2087(2)	35(1)
Re	2854(1)	6774(1)	1989(1)	17(1)
Si	1539(1)	4707(1)	3896(1)	18(1)

Table 3. Bond lengths [A] and angles [deg] for **24**.

C(1)-C(11B)	1.429(6)
C(1)-C(2)	1.435(7)
C(1)-Re	2.313(5)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.409(7)
C(2)-Re	2.298(4)
C(2)-H(2A)	0.9500
C(3)-C(3A)	1.440(6)
C(3)-Re	2.293(4)
C(3)-H(3A)	0.9500
C(3A)-C(11B)	1.434(6)
C(3A)-C(3B)	1.476(6)
C(3A)-Re	2.313(4)
C(3B)-C(4)	1.426(6)
C(3B)-C(7A)	1.434(6)
C(3B)-Cr	2.335(4)
C(4)-O(1)	1.362(5)
C(4)-C(5)	1.419(6)
C(4)-Cr	2.276(4)
C(5)-C(6)	1.429(6)
C(5)-C(18)	1.513(6)
C(5)-Cr	2.243(4)
C(6)-C(7)	1.406(7)
C(6)-C(20)	1.518(6)
C(6)-Cr	2.250(4)
C(7)-O(2)	1.379(6)
C(7)-C(7A)	1.429(6)
C(7)-Cr	2.247(5)

C(7A)-C(7B)	1.487(6)
C(7A)-Cr	2.235(4)
C(7B)-C(8)	1.402(6)
C(7B)-C(11A)	1.413(6)
C(8)-C(9)	1.384(6)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.389(7)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.377(7)
C(10)-H(10A)	0.9500
C(11)-C(11A)	1.401(6)
C(11)-H(11A)	0.9500
C(11A)-C(11B)	1.449(6)
C(11B)-Re	2.326(4)
C(12)-Si	1.855(5)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-Si	1.854(5)
C(13)-H(13C)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13A)	0.9800
C(14)-C(17)	1.529(7)
C(14)-C(16)	1.547(7)
C(14)-C(15)	1.545(6)
C(14)-Si	1.879(5)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800

C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17C)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17A)	0.9800
C(18)-C(19)	1.535(7)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19C)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19A)	0.9800
C(20)-C(21)	1.520(7)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-O(2)	1.452(6)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(3)	1.154(6)
C(23)-Re	1.921(5)
C(24)-O(4)	1.149(6)
C(24)-Re	1.919(5)
C(25)-O(5)	1.152(6)
C(25)-Re	1.915(5)
C(26)-O(6)	1.159(6)
C(26)-Cr	1.835(5)
C(27)-O(7)	1.155(5)

C(27)-Cr	1.834(5)
C(28)-O(8)	1.163(6)
C(28)-Cr	1.823(5)
C(29)-Cl(1)	1.702(7)
C(29)-Cl(2)	1.706(8)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
O(1)-Si	1.692(3)
C(11B)-C(1)-C(2)	106.9(4)
C(11B)-C(1)-Re	72.5(2)
C(2)-C(1)-Re	71.3(3)
C(11B)-C(1)-H(1A)	126.5
C(2)-C(1)-H(1A)	126.5
Re-C(1)-H(1A)	121.5
C(3)-C(2)-C(1)	109.1(4)
C(3)-C(2)-Re	71.9(2)
C(1)-C(2)-Re	72.5(3)
C(3)-C(2)-H(2A)	125.5
C(1)-C(2)-H(2A)	125.5
Re-C(2)-H(2A)	121.8
C(2)-C(3)-C(3A)	108.2(4)
C(2)-C(3)-Re	72.3(3)
C(3A)-C(3)-Re	72.6(2)
C(2)-C(3)-H(3A)	125.9
C(3A)-C(3)-H(3A)	125.9
Re-C(3)-H(3A)	121.0
C(11B)-C(3A)-C(3)	107.2(4)
C(11B)-C(3A)-C(3B)	119.8(4)
C(3)-C(3A)-C(3B)	132.5(4)
C(11B)-C(3A)-Re	72.5(2)

C(3)-C(3A)-Re	71.0(2)
C(3B)-C(3A)-Re	115.8(3)
C(4)-C(3B)-C(7A)	120.1(4)
C(4)-C(3B)-C(3A)	122.5(4)
C(7A)-C(3B)-C(3A)	117.0(4)
C(4)-C(3B)-Cr	69.7(2)
C(7A)-C(3B)-Cr	67.9(2)
C(3A)-C(3B)-Cr	142.1(3)
O(1)-C(4)-C(5)	119.9(4)
O(1)-C(4)-C(3B)	119.1(4)
C(5)-C(4)-C(3B)	120.7(4)
O(1)-C(4)-Cr	134.0(3)
C(5)-C(4)-Cr	70.4(3)
C(3B)-C(4)-Cr	74.3(2)
C(4)-C(5)-C(6)	119.1(4)
C(4)-C(5)-C(18)	119.6(4)
C(6)-C(5)-C(18)	120.8(4)
C(4)-C(5)-Cr	73.0(2)
C(6)-C(5)-Cr	71.7(2)
C(18)-C(5)-Cr	133.6(3)
C(7)-C(6)-C(5)	119.6(4)
C(7)-C(6)-C(20)	117.9(4)
C(5)-C(6)-C(20)	122.3(4)
C(7)-C(6)-Cr	71.7(3)
C(5)-C(6)-Cr	71.2(2)
C(20)-C(6)-Cr	132.7(3)
O(2)-C(7)-C(6)	117.0(4)
O(2)-C(7)-C(7A)	120.8(4)
C(6)-C(7)-C(7A)	122.2(4)
O(2)-C(7)-Cr	131.1(3)

C(6)-C(7)-Cr 71.9(3)

C(7A)-C(7)-Cr 70.9(2)

C(7)-C(7A)-C(3B) 117.2(4)

C(7)-C(7A)-C(7B) 122.4(4)

C(3B)-C(7A)-C(7B) 120.4(4)

C(7)-C(7A)-Cr 71.9(3)

C(3B)-C(7A)-Cr 75.6(2)

C(7B)-C(7A)-Cr 124.4(3)

C(8)-C(7B)-C(11A) 117.7(4)

C(8)-C(7B)-C(7A) 122.3(4)

C(11A)-C(7B)-C(7A) 119.8(4)

C(9)-C(8)-C(7B) 121.2(4)

C(9)-C(8)-H(8A) 119.4

C(7B)-C(8)-H(8A) 119.4

C(8)-C(9)-C(10) 120.4(4)

C(8)-C(9)-H(9A) 119.8

C(10)-C(9)-H(9A) 119.8

C(11)-C(10)-C(9) 119.7(4)

C(11)-C(10)-H(10A) 120.1

C(9)-C(10)-H(10A) 120.1

C(10)-C(11)-C(11A) 120.5(4)

C(10)-C(11)-H(11A) 119.7

C(11A)-C(11)-H(11A) 119.7

C(11)-C(11A)-C(7B) 120.3(4)

C(11)-C(11A)-C(11B) 121.2(4)

C(7B)-C(11A)-C(11B) 118.3(4)

C(1)-C(11B)-C(3A) 108.7(4)

C(1)-C(11B)-C(11A) 129.4(4)

C(3A)-C(11B)-C(11A) 121.9(4)

C(1)-C(11B)-Re 71.6(3)

C(3A)-C(11B)-Re	71.5(2)
C(11A)-C(11B)-Re	123.8(3)
Si-C(12)-H(12A)	109.5
Si-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
Si-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
Si-C(13)-H(13C)	109.5
Si-C(13)-H(13B)	109.5
H(13C)-C(13)-H(13B)	109.5
Si-C(13)-H(13A)	109.5
H(13C)-C(13)-H(13A)	109.5
H(13B)-C(13)-H(13A)	109.5
C(17)-C(14)-C(16)	109.0(4)
C(17)-C(14)-C(15)	109.2(4)
C(16)-C(14)-C(15)	108.6(4)
C(17)-C(14)-Si	110.9(3)
C(16)-C(14)-Si	110.5(3)
C(15)-C(14)-Si	108.5(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C) 109.5

H(16B)-C(16)-H(16C) 109.5

C(14)-C(17)-H(17C) 109.5

C(14)-C(17)-H(17B) 109.5

H(17C)-C(17)-H(17B) 109.5

C(14)-C(17)-H(17A) 109.5

H(17C)-C(17)-H(17A) 109.5

H(17B)-C(17)-H(17A) 109.5

C(5)-C(18)-C(19) 110.0(4)

C(5)-C(18)-H(18A) 109.7

C(19)-C(18)-H(18A) 109.7

C(5)-C(18)-H(18B) 109.7

C(19)-C(18)-H(18B) 109.7

H(18A)-C(18)-H(18B) 108.2

C(18)-C(19)-H(19C) 109.5

C(18)-C(19)-H(19B) 109.5

H(19C)-C(19)-H(19B) 109.5

C(18)-C(19)-H(19A) 109.5

H(19C)-C(19)-H(19A) 109.5

H(19B)-C(19)-H(19A) 109.5

C(6)-C(20)-C(21) 116.4(4)

C(6)-C(20)-H(20A) 108.2

C(21)-C(20)-H(20A) 108.2

C(6)-C(20)-H(20B) 108.2

C(21)-C(20)-H(20B) 108.2

H(20A)-C(20)-H(20B) 107.3

C(20)-C(21)-H(21A) 109.5

C(20)-C(21)-H(21B) 109.5

H(21A)-C(21)-H(21B) 109.5

C(20)-C(21)-H(21C) 109.5

H(21A)-C(21)-H(21C) 109.5

H(21B)-C(21)-H(21C) 109.5

O(2)-C(22)-H(22A) 109.5

O(2)-C(22)-H(22B) 109.5

H(22A)-C(22)-H(22B) 109.5

O(2)-C(22)-H(22C) 109.5

H(22A)-C(22)-H(22C) 109.5

H(22B)-C(22)-H(22C) 109.5

O(3)-C(23)-Re 175.7(4)

O(4)-C(24)-Re 175.3(4)

O(5)-C(25)-Re 179.6(5)

O(6)-C(26)-Cr 178.1(4)

O(7)-C(27)-Cr 179.1(4)

O(8)-C(28)-Cr 176.2(4)

Cl(1)-C(29)-Cl(2) 114.7(4)

Cl(1)-C(29)-H(29A) 108.6

Cl(2)-C(29)-H(29A) 108.6

Cl(1)-C(29)-H(29B) 108.6

Cl(2)-C(29)-H(29B) 108.6

H(29A)-C(29)-H(29B) 107.6

C(28)-Cr-C(27) 86.5(2)

C(28)-Cr-C(26) 85.1(2)

C(27)-Cr-C(26) 88.1(2)

C(28)-Cr-C(7A) 116.85(18)

C(27)-Cr-C(7A) 156.59(18)

C(26)-Cr-C(7A) 92.60(18)

C(28)-Cr-C(5) 124.4(2)

C(27)-Cr-C(5) 87.86(18)

C(26)-Cr-C(5) 149.93(19)

C(7A)-Cr-C(5) 79.88(16)

C(28)-Cr-C(7)	153.48(19)
C(27)-Cr-C(7)	119.45(18)
C(26)-Cr-C(7)	90.29(18)
C(7A)-Cr-C(7)	37.17(15)
C(5)-Cr-C(7)	66.16(17)
C(28)-Cr-C(6)	161.4(2)
C(27)-Cr-C(6)	91.06(18)
C(26)-Cr-C(6)	113.26(19)
C(7A)-Cr-C(6)	67.19(16)
C(5)-Cr-C(6)	37.09(16)
C(7)-Cr-C(6)	36.44(17)
C(28)-Cr-C(4)	98.42(18)
C(27)-Cr-C(4)	113.41(19)
C(26)-Cr-C(4)	158.32(18)
C(7A)-Cr-C(4)	66.65(15)
C(5)-Cr-C(4)	36.61(15)
C(7)-Cr-C(4)	77.01(16)
C(6)-Cr-C(4)	65.73(16)
C(28)-Cr-C(3B)	96.38(17)
C(27)-Cr-C(3B)	149.40(19)
C(26)-Cr-C(3B)	122.49(18)
C(7A)-Cr-C(3B)	36.49(14)
C(5)-Cr-C(3B)	65.34(15)
C(7)-Cr-C(3B)	64.41(15)
C(6)-Cr-C(3B)	76.60(15)
C(4)-Cr-C(3B)	36.00(15)
C(4)-O(1)-Si	136.2(3)
C(7)-O(2)-C(22)	112.5(4)
C(25)-Re-C(24)	89.7(2)
C(25)-Re-C(23)	89.8(2)

C(24)-Re-C(23)	92.3(2)
C(25)-Re-C(3)	123.0(2)
C(24)-Re-C(3)	146.51(19)
C(23)-Re-C(3)	94.44(19)
C(25)-Re-C(2)	97.8(2)
C(24)-Re-C(2)	144.41(19)
C(23)-Re-C(2)	122.28(19)
C(3)-Re-C(2)	35.74(17)
C(25)-Re-C(3A)	157.7(2)
C(24)-Re-C(3A)	110.08(18)
C(23)-Re-C(3A)	99.32(18)
C(3)-Re-C(3A)	36.43(15)
C(2)-Re-C(3A)	60.04(16)
C(25)-Re-C(1)	104.44(19)
C(24)-Re-C(1)	108.17(18)
C(23)-Re-C(1)	154.80(19)
C(3)-Re-C(1)	60.37(17)
C(2)-Re-C(1)	36.27(17)
C(3A)-Re-C(1)	60.37(15)
C(25)-Re-C(11B)	137.63(19)
C(24)-Re-C(11B)	91.76(17)
C(23)-Re-C(11B)	132.36(18)
C(3)-Re-C(11B)	60.08(16)
C(2)-Re-C(11B)	59.72(16)
C(3A)-Re-C(11B)	36.00(15)
C(1)-Re-C(11B)	35.89(14)
O(1)-Si-C(13)	109.80(19)
O(1)-Si-C(12)	112.56(19)
C(13)-Si-C(12)	108.6(2)
O(1)-Si-C(14)	103.97(18)

C(13)-Si-C(14)	111.1(2)
C(12)-Si-C(14)	110.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **24**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	25(3)	17(2)	26(3)	6(2)	10(2)	4(2)
C(2)	29(2)	17(3)	32(3)	-1(2)	15(2)	7(2)
C(3)	22(2)	19(2)	23(3)	-2(2)	12(2)	3(2)
C(3A)	11(2)	17(2)	19(2)	0(2)	6(2)	1(2)
C(3B)	11(2)	17(2)	18(2)	-1(2)	5(2)	-1(2)
C(4)	9(2)	18(2)	18(2)	0(2)	3(2)	-2(2)
C(5)	14(2)	17(2)	19(2)	2(2)	3(2)	-3(2)
C(6)	18(2)	17(2)	22(3)	2(2)	8(2)	0(2)
C(7)	14(2)	19(3)	22(2)	-1(2)	8(2)	1(2)
C(7A)	13(2)	15(2)	18(2)	1(2)	7(2)	-3(2)
C(7B)	13(2)	21(2)	17(2)	0(2)	6(2)	-3(2)
C(8)	23(2)	20(3)	21(2)	-1(2)	11(2)	0(2)
C(9)	25(2)	28(3)	20(2)	-4(2)	10(2)	-5(2)
C(10)	20(2)	34(3)	15(2)	3(2)	4(2)	-1(2)
C(11)	19(2)	24(3)	22(2)	4(2)	9(2)	3(2)
C(11A)	11(2)	21(2)	19(2)	2(2)	5(2)	-1(2)
C(11B)	12(2)	18(2)	21(2)	2(2)	6(2)	0(2)
C(12)	26(3)	32(3)	21(3)	2(2)	10(2)	-5(2)
C(13)	20(2)	37(3)	26(3)	2(2)	9(2)	4(2)

C(14)	27(3)	26(3)	21(3)	-4(2)	9(2)	-3(2)
C(15)	41(3)	42(3)	22(3)	-9(2)	16(2)	-1(2)
C(16)	30(3)	45(4)	22(3)	-8(2)	1(2)	4(2)
C(17)	56(4)	37(3)	28(3)	-13(3)	14(3)	-17(3)
C(18)	23(3)	23(3)	19(3)	3(2)	4(2)	2(2)
C(19)	19(3)	40(3)	24(3)	0(2)	-6(2)	2(2)
C(20)	26(2)	23(3)	26(3)	3(2)	10(2)	9(2)
C(21)	38(3)	19(3)	41(3)	4(2)	15(2)	9(2)
C(22)	27(3)	42(3)	41(3)	7(3)	24(3)	8(2)
C(23)	28(3)	23(3)	33(3)	0(2)	12(2)	-6(2)
C(24)	16(2)	42(3)	26(3)	-9(2)	3(2)	-16(2)
C(25)	33(3)	30(3)	28(3)	7(2)	2(2)	-2(2)
C(26)	25(2)	20(3)	25(3)	3(2)	11(2)	-6(2)
C(27)	19(2)	23(3)	18(2)	-2(2)	5(2)	-1(2)
C(28)	24(3)	23(3)	19(3)	5(2)	5(2)	-4(2)
C(29)	79(5)	45(5)	136(8)	-27(5)	62(6)	-22(4)
Cl(1)	120(2)	44(1)	139(2)	28(1)	73(2)	12(1)
Cl(2)	95(2)	46(1)	75(1)	-14(1)	-19(1)	13(1)
Cr	15(1)	15(1)	15(1)	1(1)	5(1)	-1(1)
O(1)	20(2)	18(2)	16(2)	-2(1)	8(1)	-1(1)
O(2)	28(2)	21(2)	28(2)	1(2)	16(2)	7(1)
O(3)	33(2)	56(3)	30(2)	13(2)	-1(2)	2(2)
O(4)	31(2)	78(3)	44(2)	-28(2)	22(2)	-18(2)
O(5)	62(3)	24(2)	57(3)	3(2)	3(2)	-20(2)
O(6)	47(2)	37(2)	23(2)	-9(2)	12(2)	-20(2)
O(7)	38(2)	22(2)	30(2)	8(2)	11(2)	-3(2)
O(8)	21(2)	47(2)	40(2)	13(2)	17(2)	1(2)
Re	19(1)	14(1)	17(1)	0(1)	5(1)	-2(1)
Si	18(1)	22(1)	15(1)	1(1)	6(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **24**.

	x	y	z	U(eq)
H(1A)	994	7356	801	27
H(2A)	1211	7790	2147	30
H(3A)	1816	6349	2971	25
H(8A)	1882	3180	253	25
H(9A)	1040	3675	-981	29
H(10A)	480	5239	-1239	29
H(11A)	684	6282	-252	26
H(12A)	1076	3098	3615	39
H(12B)	691	3476	4241	39
H(12C)	1827	3191	4474	39
H(13C)	482	5998	3324	41
H(13B)	-136	5175	3520	41
H(13A)	147	5081	2795	41
H(15A)	1822	5747	5716	51
H(15B)	1387	4731	5379	51
H(15C)	876	5677	4943	51
H(16A)	3010	4186	5379	53
H(16B)	3473	5170	5771	53
H(16C)	3609	4839	5018	53
H(17C)	2855	6364	4365	61
H(17B)	2785	6696	5141	61
H(17A)	1821	6716	4377	61
H(18A)	3597	2405	3923	28

H(18B)	3136	3312	4175	28
H(19C)	4878	3343	4804	48
H(19B)	4546	4229	4241	48
H(19A)	5009	3308	4014	48
H(20A)	4335	2045	3238	30
H(20B)	4595	2319	2528	30
H(21A)	3328	1281	1767	49
H(21B)	3117	984	2497	49
H(21C)	4154	726	2444	49
H(22A)	4525	3584	1561	51
H(22B)	3682	3995	815	51
H(22C)	4237	3029	779	51
H(29A)	-2853	4529	514	96
H(29B)	-2465	4728	1399	96

Table 6. Torsion angles [deg] for **24**.

C(11B)-C(1)-C(2)-C(3)	1.2(5)
Re-C(1)-C(2)-C(3)	-63.1(3)
C(11B)-C(1)-C(2)-Re	64.2(3)
C(1)-C(2)-C(3)-C(3A)	-0.8(5)
Re-C(2)-C(3)-C(3A)	-64.2(3)
C(1)-C(2)-C(3)-Re	63.4(3)
C(2)-C(3)-C(3A)-C(11B)	0.1(5)
Re-C(3)-C(3A)-C(11B)	-63.9(3)
C(2)-C(3)-C(3A)-C(3B)	172.0(4)
Re-C(3)-C(3A)-C(3B)	108.0(4)
C(2)-C(3)-C(3A)-Re	64.0(3)
C(11B)-C(3A)-C(3B)-C(4)	177.3(4)

C(3)-C(3A)-C(3B)-C(4)	6.2(7)
Re-C(3A)-C(3B)-C(4)	93.5(4)
C(11B)-C(3A)-C(3B)-C(7A)	4.1(5)
C(3)-C(3A)-C(3B)-C(7A)	-167.0(4)
Re-C(3A)-C(3B)-C(7A)	-79.7(4)
C(11B)-C(3A)-C(3B)-Cr	-84.0(6)
C(3)-C(3A)-C(3B)-Cr	104.8(6)
Re-C(3A)-C(3B)-Cr	-167.8(3)
C(7A)-C(3B)-C(4)-O(1)	-179.3(3)
C(3A)-C(3B)-C(4)-O(1)	7.7(6)
Cr-C(3B)-C(4)-O(1)	-132.0(3)
C(7A)-C(3B)-C(4)-C(5)	7.8(6)
C(3A)-C(3B)-C(4)-C(5)	-165.2(4)
Cr-C(3B)-C(4)-C(5)	55.2(4)
C(7A)-C(3B)-C(4)-Cr	-47.4(3)
C(3A)-C(3B)-C(4)-Cr	139.7(4)
O(1)-C(4)-C(5)-C(6)	-172.9(4)
C(3B)-C(4)-C(5)-C(6)	-0.1(6)
Cr-C(4)-C(5)-C(6)	56.9(3)
O(1)-C(4)-C(5)-C(18)	-0.8(6)
C(3B)-C(4)-C(5)-C(18)	172.0(4)
Cr-C(4)-C(5)-C(18)	-131.0(4)
O(1)-C(4)-C(5)-Cr	130.2(4)
C(3B)-C(4)-C(5)-Cr	-57.0(4)
C(4)-C(5)-C(6)-C(7)	-2.7(6)
C(18)-C(5)-C(6)-C(7)	-174.7(4)
Cr-C(5)-C(6)-C(7)	54.8(4)
C(4)-C(5)-C(6)-C(20)	173.3(4)
C(18)-C(5)-C(6)-C(20)	1.3(6)
Cr-C(5)-C(6)-C(20)	-129.2(4)

C(4)-C(5)-C(6)-Cr	-57.5(3)
C(18)-C(5)-C(6)-Cr	130.5(4)
C(5)-C(6)-C(7)-O(2)	177.8(4)
C(20)-C(6)-C(7)-O(2)	1.7(6)
Cr-C(6)-C(7)-O(2)	-127.6(4)
C(5)-C(6)-C(7)-C(7A)	-2.4(6)
C(20)-C(6)-C(7)-C(7A)	-178.5(4)
Cr-C(6)-C(7)-C(7A)	52.2(4)
C(5)-C(6)-C(7)-Cr	-54.6(4)
C(20)-C(6)-C(7)-Cr	129.3(4)
O(2)-C(7)-C(7A)-C(3B)	-170.4(4)
C(6)-C(7)-C(7A)-C(3B)	9.8(6)
Cr-C(7)-C(7A)-C(3B)	62.4(3)
O(2)-C(7)-C(7A)-C(7B)	7.4(6)
C(6)-C(7)-C(7A)-C(7B)	-172.4(4)
Cr-C(7)-C(7A)-C(7B)	-119.7(4)
O(2)-C(7)-C(7A)-Cr	127.2(4)
C(6)-C(7)-C(7A)-Cr	-52.7(4)
C(4)-C(3B)-C(7A)-C(7)	-12.3(6)
C(3A)-C(3B)-C(7A)-C(7)	161.0(4)
Cr-C(3B)-C(7A)-C(7)	-60.5(3)
C(4)-C(3B)-C(7A)-C(7B)	169.8(4)
C(3A)-C(3B)-C(7A)-C(7B)	-16.9(5)
Cr-C(3B)-C(7A)-C(7B)	121.7(4)
C(4)-C(3B)-C(7A)-Cr	48.1(3)
C(3A)-C(3B)-C(7A)-Cr	-138.5(3)
C(7)-C(7A)-C(7B)-C(8)	23.1(6)
C(3B)-C(7A)-C(7B)-C(8)	-159.1(4)
Cr-C(7A)-C(7B)-C(8)	-66.2(5)
C(7)-C(7A)-C(7B)-C(11A)	-160.2(4)

C(3B)-C(7A)-C(7B)-C(11A)	17.5(6)
Cr-C(7A)-C(7B)-C(11A)	110.5(4)
C(11A)-C(7B)-C(8)-C(9)	1.2(6)
C(7A)-C(7B)-C(8)-C(9)	177.8(4)
C(7B)-C(8)-C(9)-C(10)	1.2(7)
C(8)-C(9)-C(10)-C(11)	-2.1(7)
C(9)-C(10)-C(11)-C(11A)	0.6(7)
C(10)-C(11)-C(11A)-C(7B)	1.7(6)
C(10)-C(11)-C(11A)-C(11B)	-172.9(4)
C(8)-C(7B)-C(11A)-C(11)	-2.6(6)
C(7A)-C(7B)-C(11A)-C(11)	-179.4(4)
C(8)-C(7B)-C(11A)-C(11B)	172.2(4)
C(7A)-C(7B)-C(11A)-C(11B)	-4.5(6)
C(2)-C(1)-C(11B)-C(3A)	-1.1(5)
Re-C(1)-C(11B)-C(3A)	62.3(3)
C(2)-C(1)-C(11B)-C(11A)	177.6(4)
Re-C(1)-C(11B)-C(11A)	-119.0(4)
C(2)-C(1)-C(11B)-Re	-63.4(3)
C(3)-C(3A)-C(11B)-C(1)	0.6(5)
C(3B)-C(3A)-C(11B)-C(1)	-172.5(4)
Re-C(3A)-C(11B)-C(1)	-62.3(3)
C(3)-C(3A)-C(11B)-C(11A)	-178.1(4)
C(3B)-C(3A)-C(11B)-C(11A)	8.7(6)
Re-C(3A)-C(11B)-C(11A)	118.9(4)
C(3)-C(3A)-C(11B)-Re	63.0(3)
C(3B)-C(3A)-C(11B)-Re	-110.2(3)
C(11)-C(11A)-C(11B)-C(1)	-12.1(7)
C(7B)-C(11A)-C(11B)-C(1)	173.1(4)
C(11)-C(11A)-C(11B)-C(3A)	166.4(4)
C(7B)-C(11A)-C(11B)-C(3A)	-8.4(6)

C(11)-C(11A)-C(11B)-Re	-105.5(4)
C(7B)-C(11A)-C(11B)-Re	79.8(5)
C(4)-C(5)-C(18)-C(19)	-91.6(5)
C(6)-C(5)-C(18)-C(19)	80.4(5)
Cr-C(5)-C(18)-C(19)	174.1(4)
C(7)-C(6)-C(20)-C(21)	-67.8(6)
C(5)-C(6)-C(20)-C(21)	116.2(5)
Cr-C(6)-C(20)-C(21)	22.5(7)
O(8)-C(28)-Cr-C(27)	-54(7)
O(8)-C(28)-Cr-C(26)	34(7)
O(8)-C(28)-Cr-C(7A)	125(7)
O(8)-C(28)-Cr-C(5)	-139(7)
O(8)-C(28)-Cr-C(7)	115(6)
O(8)-C(28)-Cr-C(6)	-137(6)
O(8)-C(28)-Cr-C(4)	-167(7)
O(8)-C(28)-Cr-C(3B)	156(7)
O(7)-C(27)-Cr-C(28)	-60(27)
O(7)-C(27)-Cr-C(26)	-145(27)
O(7)-C(27)-Cr-C(7A)	123(27)
O(7)-C(27)-Cr-C(5)	65(27)
O(7)-C(27)-Cr-C(7)	126(27)
O(7)-C(27)-Cr-C(6)	102(27)
O(7)-C(27)-Cr-C(4)	38(27)
O(7)-C(27)-Cr-C(3B)	37(27)
O(6)-C(26)-Cr-C(28)	11(13)
O(6)-C(26)-Cr-C(27)	98(13)
O(6)-C(26)-Cr-C(7A)	-106(13)
O(6)-C(26)-Cr-C(5)	-180(100)
O(6)-C(26)-Cr-C(7)	-143(13)
O(6)-C(26)-Cr-C(6)	-172(13)

O(6)-C(26)-Cr-C(4)	-89(13)
O(6)-C(26)-Cr-C(3B)	-83(13)
C(7)-C(7A)-Cr-C(28)	-172.8(3)
C(3B)-C(7A)-Cr-C(28)	61.6(3)
C(7B)-C(7A)-Cr-C(28)	-55.5(4)
C(7)-C(7A)-Cr-C(27)	4.1(6)
C(3B)-C(7A)-Cr-C(27)	-121.4(5)
C(7B)-C(7A)-Cr-C(27)	121.4(5)
C(7)-C(7A)-Cr-C(26)	-87.0(3)
C(3B)-C(7A)-Cr-C(26)	147.4(3)
C(7B)-C(7A)-Cr-C(26)	30.3(4)
C(7)-C(7A)-Cr-C(5)	63.6(3)
C(3B)-C(7A)-Cr-C(5)	-61.9(2)
C(7B)-C(7A)-Cr-C(5)	-179.1(4)
C(3B)-C(7A)-Cr-C(7)	-125.5(4)
C(7B)-C(7A)-Cr-C(7)	117.3(5)
C(7)-C(7A)-Cr-C(6)	27.1(3)
C(3B)-C(7A)-Cr-C(6)	-98.4(3)
C(7B)-C(7A)-Cr-C(6)	144.4(4)
C(7)-C(7A)-Cr-C(4)	99.4(3)
C(3B)-C(7A)-Cr-C(4)	-26.1(2)
C(7B)-C(7A)-Cr-C(4)	-143.3(4)
C(7)-C(7A)-Cr-C(3B)	125.5(4)
C(7B)-C(7A)-Cr-C(3B)	-117.2(4)
C(4)-C(5)-Cr-C(28)	-51.5(3)
C(6)-C(5)-Cr-C(28)	178.9(3)
C(18)-C(5)-Cr-C(28)	63.4(5)
C(4)-C(5)-Cr-C(27)	-135.8(3)
C(6)-C(5)-Cr-C(27)	94.6(3)
C(18)-C(5)-Cr-C(27)	-20.9(5)

C(4)-C(5)-Cr-C(26)	141.7(4)
C(6)-C(5)-Cr-C(26)	12.1(5)
C(18)-C(5)-Cr-C(26)	-103.4(5)
C(4)-C(5)-Cr-C(7A)	64.2(3)
C(6)-C(5)-Cr-C(7A)	-65.4(3)
C(18)-C(5)-Cr-C(7A)	179.1(5)
C(4)-C(5)-Cr-C(7)	100.5(3)
C(6)-C(5)-Cr-C(7)	-29.1(3)
C(18)-C(5)-Cr-C(7)	-144.6(5)
C(4)-C(5)-Cr-C(6)	129.6(4)
C(18)-C(5)-Cr-C(6)	-115.5(5)
C(6)-C(5)-Cr-C(4)	-129.6(4)
C(18)-C(5)-Cr-C(4)	114.9(5)
C(4)-C(5)-Cr-C(3B)	29.0(2)
C(6)-C(5)-Cr-C(3B)	-100.6(3)
C(18)-C(5)-Cr-C(3B)	143.9(5)
O(2)-C(7)-Cr-C(28)	-100.3(6)
C(6)-C(7)-Cr-C(28)	149.3(4)
C(7A)-C(7)-Cr-C(28)	14.4(6)
O(2)-C(7)-Cr-C(27)	67.2(5)
C(6)-C(7)-Cr-C(27)	-43.2(3)
C(7A)-C(7)-Cr-C(27)	-178.1(3)
O(2)-C(7)-Cr-C(26)	-20.8(4)
C(6)-C(7)-Cr-C(26)	-131.2(3)
C(7A)-C(7)-Cr-C(26)	93.9(3)
O(2)-C(7)-Cr-C(7A)	-114.7(5)
C(6)-C(7)-Cr-C(7A)	134.9(4)
O(2)-C(7)-Cr-C(5)	139.9(5)
C(6)-C(7)-Cr-C(5)	29.6(3)
C(7A)-C(7)-Cr-C(5)	-105.3(3)

O(2)-C(7)-Cr-C(6)	110.4(5)
C(7A)-C(7)-Cr-C(6)	-134.9(4)
O(2)-C(7)-Cr-C(4)	176.9(4)
C(6)-C(7)-Cr-C(4)	66.6(3)
C(7A)-C(7)-Cr-C(4)	-68.4(3)
O(2)-C(7)-Cr-C(3B)	-147.2(5)
C(6)-C(7)-Cr-C(3B)	102.5(3)
C(7A)-C(7)-Cr-C(3B)	-32.5(2)
C(7)-C(6)-Cr-C(28)	-134.3(6)
C(5)-C(6)-Cr-C(28)	-2.8(7)
C(20)-C(6)-Cr-C(28)	114.2(7)
C(7)-C(6)-Cr-C(27)	143.4(3)
C(5)-C(6)-Cr-C(27)	-85.0(3)
C(20)-C(6)-Cr-C(27)	32.0(5)
C(7)-C(6)-Cr-C(26)	55.0(3)
C(5)-C(6)-Cr-C(26)	-173.4(3)
C(20)-C(6)-Cr-C(26)	-56.4(5)
C(7)-C(6)-Cr-C(7A)	-27.6(3)
C(5)-C(6)-Cr-C(7A)	103.9(3)
C(20)-C(6)-Cr-C(7A)	-139.1(5)
C(7)-C(6)-Cr-C(5)	-131.5(4)
C(20)-C(6)-Cr-C(5)	117.0(6)
C(5)-C(6)-Cr-C(7)	131.5(4)
C(20)-C(6)-Cr-C(7)	-111.5(6)
C(7)-C(6)-Cr-C(4)	-101.3(3)
C(5)-C(6)-Cr-C(4)	30.3(2)
C(20)-C(6)-Cr-C(4)	147.3(5)
C(7)-C(6)-Cr-C(3B)	-64.9(3)
C(5)-C(6)-Cr-C(3B)	66.7(3)
C(20)-C(6)-Cr-C(3B)	-176.3(5)

O(1)-C(4)-Cr-C(28)	26.2(4)
C(5)-C(4)-Cr-C(28)	139.2(3)
C(3B)-C(4)-Cr-C(28)	-89.3(3)
O(1)-C(4)-Cr-C(27)	-63.7(4)
C(5)-C(4)-Cr-C(27)	49.4(3)
C(3B)-C(4)-Cr-C(27)	-179.1(2)
O(1)-C(4)-Cr-C(26)	124.1(5)
C(5)-C(4)-Cr-C(26)	-122.9(5)
C(3B)-C(4)-Cr-C(26)	8.6(6)
O(1)-C(4)-Cr-C(7A)	141.9(4)
C(5)-C(4)-Cr-C(7A)	-105.1(3)
C(3B)-C(4)-Cr-C(7A)	26.4(2)
O(1)-C(4)-Cr-C(5)	-113.0(5)
C(3B)-C(4)-Cr-C(5)	131.5(4)
O(1)-C(4)-Cr-C(7)	179.6(4)
C(5)-C(4)-Cr-C(7)	-67.4(3)
C(3B)-C(4)-Cr-C(7)	64.1(2)
O(1)-C(4)-Cr-C(6)	-143.7(5)
C(5)-C(4)-Cr-C(6)	-30.6(3)
C(3B)-C(4)-Cr-C(6)	100.8(3)
O(1)-C(4)-Cr-C(3B)	115.5(5)
C(5)-C(4)-Cr-C(3B)	-131.5(4)
C(4)-C(3B)-Cr-C(28)	95.6(3)
C(7A)-C(3B)-Cr-C(28)	-127.8(3)
C(3A)-C(3B)-Cr-C(28)	-21.7(5)
C(4)-C(3B)-Cr-C(27)	1.6(4)
C(7A)-C(3B)-Cr-C(27)	138.2(3)
C(3A)-C(3B)-Cr-C(27)	-115.7(5)
C(4)-C(3B)-Cr-C(26)	-176.2(3)
C(7A)-C(3B)-Cr-C(26)	-39.6(3)

C(3A)-C(3B)-Cr-C(26)	66.5(5)
C(4)-C(3B)-Cr-C(7A)	-136.6(3)
C(3A)-C(3B)-Cr-C(7A)	106.1(6)
C(4)-C(3B)-Cr-C(5)	-29.5(2)
C(7A)-C(3B)-Cr-C(5)	107.2(3)
C(3A)-C(3B)-Cr-C(5)	-146.7(5)
C(4)-C(3B)-Cr-C(7)	-103.6(3)
C(7A)-C(3B)-Cr-C(7)	33.0(2)
C(3A)-C(3B)-Cr-C(7)	139.1(5)
C(4)-C(3B)-Cr-C(6)	-67.0(2)
C(7A)-C(3B)-Cr-C(6)	69.6(2)
C(3A)-C(3B)-Cr-C(6)	175.7(5)
C(7A)-C(3B)-Cr-C(4)	136.6(3)
C(3A)-C(3B)-Cr-C(4)	-117.3(6)
C(5)-C(4)-O(1)-Si	-85.9(5)
C(3B)-C(4)-O(1)-Si	101.1(5)
Cr-C(4)-O(1)-Si	5.1(6)
C(6)-C(7)-O(2)-C(22)	-103.6(5)
C(7A)-C(7)-O(2)-C(22)	76.5(5)
Cr-C(7)-O(2)-C(22)	167.4(4)
O(5)-C(25)-Re-C(24)	143(66)
O(5)-C(25)-Re-C(23)	-125(66)
O(5)-C(25)-Re-C(3)	-29(66)
O(5)-C(25)-Re-C(2)	-2(66)
O(5)-C(25)-Re-C(3A)	-10(67)
O(5)-C(25)-Re-C(1)	34(66)
O(5)-C(25)-Re-C(11B)	51(66)
O(4)-C(24)-Re-C(25)	-143(6)
O(4)-C(24)-Re-C(23)	127(6)
O(4)-C(24)-Re-C(3)	26(7)

O(4)-C(24)-Re-C(2)	-40(7)
O(4)-C(24)-Re-C(3A)	27(7)
O(4)-C(24)-Re-C(1)	-38(7)
O(4)-C(24)-Re-C(11B)	-5(6)
O(3)-C(23)-Re-C(25)	125(6)
O(3)-C(23)-Re-C(24)	-146(6)
O(3)-C(23)-Re-C(3)	2(6)
O(3)-C(23)-Re-C(2)	26(7)
O(3)-C(23)-Re-C(3A)	-35(6)
O(3)-C(23)-Re-C(1)	-1(7)
O(3)-C(23)-Re-C(11B)	-51(7)
C(2)-C(3)-Re-C(25)	51.3(4)
C(3A)-C(3)-Re-C(25)	167.6(3)
C(2)-C(3)-Re-C(24)	-115.0(4)
C(3A)-C(3)-Re-C(24)	1.3(5)
C(2)-C(3)-Re-C(23)	144.0(3)
C(3A)-C(3)-Re-C(23)	-99.7(3)
C(3A)-C(3)-Re-C(2)	116.3(4)
C(2)-C(3)-Re-C(3A)	-116.3(4)
C(2)-C(3)-Re-C(1)	-37.1(3)
C(3A)-C(3)-Re-C(1)	79.2(3)
C(2)-C(3)-Re-C(11B)	-78.7(3)
C(3A)-C(3)-Re-C(11B)	37.6(2)
C(3)-C(2)-Re-C(25)	-138.7(3)
C(1)-C(2)-Re-C(25)	103.7(3)
C(3)-C(2)-Re-C(24)	120.8(4)
C(1)-C(2)-Re-C(24)	3.2(5)
C(3)-C(2)-Re-C(23)	-43.9(4)
C(1)-C(2)-Re-C(23)	-161.5(3)
C(1)-C(2)-Re-C(3)	-117.6(4)

C(3)-C(2)-Re-C(3A)	37.9(3)
C(1)-C(2)-Re-C(3A)	-79.7(3)
C(3)-C(2)-Re-C(1)	117.6(4)
C(3)-C(2)-Re-C(11B)	79.8(3)
C(1)-C(2)-Re-C(11B)	-37.8(3)
C(11B)-C(3A)-Re-C(25)	87.6(5)
C(3)-C(3A)-Re-C(25)	-28.2(6)
C(3B)-C(3A)-Re-C(25)	-157.1(5)
C(11B)-C(3A)-Re-C(24)	-63.4(3)
C(3)-C(3A)-Re-C(24)	-179.2(3)
C(3B)-C(3A)-Re-C(24)	51.9(4)
C(11B)-C(3A)-Re-C(23)	-159.3(3)
C(3)-C(3A)-Re-C(23)	84.8(3)
C(3B)-C(3A)-Re-C(23)	-44.1(4)
C(11B)-C(3A)-Re-C(3)	115.8(4)
C(3B)-C(3A)-Re-C(3)	-128.9(4)
C(11B)-C(3A)-Re-C(2)	78.6(3)
C(3)-C(3A)-Re-C(2)	-37.2(3)
C(3B)-C(3A)-Re-C(2)	-166.1(4)
C(11B)-C(3A)-Re-C(1)	36.6(2)
C(3)-C(3A)-Re-C(1)	-79.2(3)
C(3B)-C(3A)-Re-C(1)	151.9(4)
C(3)-C(3A)-Re-C(11B)	-115.8(4)
C(3B)-C(3A)-Re-C(11B)	115.3(4)
C(11B)-C(1)-Re-C(25)	161.0(3)
C(2)-C(1)-Re-C(25)	-83.5(3)
C(11B)-C(1)-Re-C(24)	66.5(3)
C(2)-C(1)-Re-C(24)	-178.1(3)
C(11B)-C(1)-Re-C(23)	-76.3(5)
C(2)-C(1)-Re-C(23)	39.2(6)

C(11B)-C(1)-Re-C(3)	-78.9(3)
C(2)-C(1)-Re-C(3)	36.5(3)
C(11B)-C(1)-Re-C(2)	-115.4(4)
C(11B)-C(1)-Re-C(3A)	-36.7(2)
C(2)-C(1)-Re-C(3A)	78.7(3)
C(2)-C(1)-Re-C(11B)	115.4(4)
C(1)-C(11B)-Re-C(25)	-27.8(4)
C(3A)-C(11B)-Re-C(25)	-145.7(3)
C(11A)-C(11B)-Re-C(25)	97.8(4)
C(1)-C(11B)-Re-C(24)	-119.3(3)
C(3A)-C(11B)-Re-C(24)	122.8(3)
C(11A)-C(11B)-Re-C(24)	6.3(4)
C(1)-C(11B)-Re-C(23)	146.0(3)
C(3A)-C(11B)-Re-C(23)	28.1(4)
C(11A)-C(11B)-Re-C(23)	-88.4(4)
C(1)-C(11B)-Re-C(3)	79.8(3)
C(3A)-C(11B)-Re-C(3)	-38.1(2)
C(11A)-C(11B)-Re-C(3)	-154.6(4)
C(1)-C(11B)-Re-C(2)	38.2(3)
C(3A)-C(11B)-Re-C(2)	-79.6(3)
C(11A)-C(11B)-Re-C(2)	163.9(4)
C(1)-C(11B)-Re-C(3A)	117.8(4)
C(11A)-C(11B)-Re-C(3A)	-116.5(5)
C(3A)-C(11B)-Re-C(1)	-117.8(4)
C(11A)-C(11B)-Re-C(1)	125.7(5)
C(4)-O(1)-Si-C(13)	-82.3(4)
C(4)-O(1)-Si-C(12)	38.9(4)
C(4)-O(1)-Si-C(14)	158.8(4)
C(17)-C(14)-Si-O(1)	58.6(4)
C(16)-C(14)-Si-O(1)	-62.4(4)

C(15)-C(14)-Si-O(1)	178.6(3)
C(17)-C(14)-Si-C(13)	-59.4(4)
C(16)-C(14)-Si-C(13)	179.6(3)
C(15)-C(14)-Si-C(13)	60.6(4)
C(17)-C(14)-Si-C(12)	179.8(4)
C(16)-C(14)-Si-C(12)	58.7(4)
C(15)-C(14)-Si-C(12)	-60.3(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **24** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.11 *Syn*-tricarbonyl-{tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(9,10-diethyl-8-methoxy-11-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*c*,*e*]indenyl)chromium[ŋ^5-1,2,3,3a,11b]}rhenium (25)

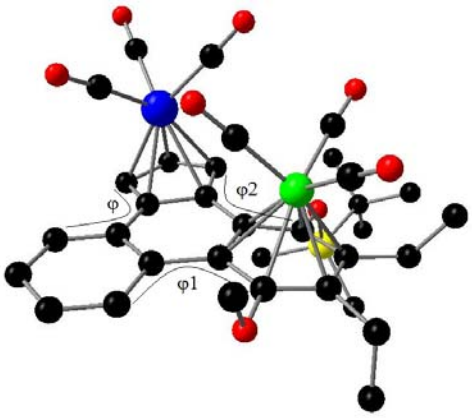


Table 1. Crystal data and structure refinement for **25**.

Empirical formula	C72 H80 Cr2 O17 Re2 Si2
Formula weight	1749.96
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 11.6018(2) A alpha = 90 deg.
	b = 15.0366(5) A beta = 98.7583(15) deg.

c = 21.1396(6) A gamma = 90 deg.

Volume	3644.84(17) A^3
Z, Calculated density	2, 1.594 Mg/m^3
Absorption coefficient	3.669 mm^-1
F(000)	1748
Crystal size	0.64 x 0.14 x 0.14 mm
Theta range for data collection	2.71 to 29.00 deg.
Limiting indices	-15<=h<=15, -20<=k<=18, -28<=l<=28
Reflections collected / unique	25464 / 9660 [R(int) = 0.0461]
Completeness to theta = 29.00	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.45526 and 0.41778
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9660 / 31 / 459
Goodness-of-fit on F^2	0.918
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0470
R indices (all data)	R1 = 0.0453, wR2 = 0.0501
Largest diff. peak and hole	0.774 and -0.774 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **25**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6870(2)	259(2)	7250(1)	20(1)
C(2)	6245(2)	1036(2)	7029(1)	19(1)
C(3)	6079(2)	1571(2)	7553(1)	15(1)
C(3A)	6555(2)	1101(2)	8130(1)	14(1)
C(3B)	6460(2)	1239(2)	8809(1)	13(1)

C(4)	5680(2)	1886(2)	9002(1)	14(1)
C(5)	5630(2)	2073(2)	9655(1)	14(1)
C(6)	6283(2)	1517(2)	10121(1)	14(1)
C(7)	6977(2)	812(2)	9930(1)	14(1)
C(7A)	7071(2)	638(2)	9282(1)	14(1)
C(7B)	7680(2)	-159(2)	9062(1)	14(1)
C(8)	8174(2)	-831(2)	9485(1)	18(1)
C(9)	8706(2)	-1562(2)	9266(1)	21(1)
C(10)	8783(2)	-1670(2)	8627(1)	22(1)
C(11)	8244(2)	-1049(2)	8197(1)	19(1)
C(11A)	7683(2)	-302(2)	8404(1)	14(1)
C(11B)	7087(2)	311(2)	7937(1)	15(1)
C(12)	3466(2)	1156(2)	7708(2)	34(1)
C(13)	2774(2)	1782(2)	8935(1)	28(1)
C(14)	3007(2)	3170(2)	7874(2)	27(1)
C(15)	3674(2)	3419(2)	7324(1)	31(1)
C(16)	1712(2)	3030(3)	7595(2)	56(1)
C(17)	3124(3)	3950(2)	8351(2)	54(1)
C(18)	4872(2)	2821(2)	9849(1)	21(1)
C(19)	5506(3)	3652(2)	10138(2)	30(1)
C(20)	6138(2)	1579(2)	10819(1)	18(1)
C(21)	5188(2)	928(2)	10954(1)	26(1)
C(22)	8705(2)	476(2)	10666(1)	23(1)
C(23)	8660(2)	2587(2)	7868(2)	23(1)
C(24)	9571(2)	968(2)	7734(1)	22(1)
C(25)	8530(2)	1860(2)	6726(2)	29(1)
C(26)	7420(2)	3182(2)	9120(1)	21(1)
C(27)	8975(2)	1889(2)	9323(1)	18(1)
C(28)	8242(2)	2642(2)	10264(1)	21(1)
Cr	7516(1)	2099(1)	9533(1)	14(1)

O(1)	4989(1)	2362(1)	8544(1)	15(1)
O(2)	7497(1)	274(1)	10421(1)	17(1)
O(3)	9032(2)	3248(2)	8067(1)	33(1)
O(4)	10462(2)	629(2)	7875(1)	33(1)
O(5)	8807(2)	2082(2)	6249(1)	49(1)
O(6)	7294(2)	3862(2)	8862(1)	37(1)
O(7)	9892(2)	1745(2)	9197(1)	31(1)
O(8)	8698(2)	2967(2)	10736(1)	35(1)
Re	8050(1)	1476(1)	7501(1)	16(1)
Si	3568(1)	2115(1)	8271(1)	19(1)
C(29)	3788(11)	-396(11)	5167(8)	143(6)
C(30)	4622(9)	-350(8)	4576(6)	100(4)
O(9)	5586(9)	101(8)	5009(7)	168(4)
C(31)	5885(11)	943(9)	4720(8)	146(5)
C(32)	7087(8)	930(7)	5158(5)	97(4)

Table 3. Bond lengths [A] and angles [deg] for **25**.

C(1)-C(2)	1.416(4)
C(1)-C(11B)	1.438(4)
C(1)-Re	2.299(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.406(4)
C(2)-Re	2.277(3)
C(2)-H(2A)	0.9500
C(3)-C(3A)	1.444(4)
C(3)-Re	2.311(2)
C(3)-H(3A)	0.9500
C(3A)-C(11B)	1.426(4)

C(3A)-C(3B)	1.471(3)
C(3A)-Re	2.407(2)
C(3B)-C(4)	1.430(4)
C(3B)-C(7A)	1.450(4)
C(3B)-Cr	2.224(3)
C(4)-O(1)	1.362(3)
C(4)-C(5)	1.420(3)
C(4)-Cr	2.274(2)
C(5)-C(6)	1.420(4)
C(5)-C(18)	1.521(4)
C(5)-Cr	2.243(2)
C(6)-C(7)	1.426(4)
C(6)-C(20)	1.515(3)
C(6)-Cr	2.213(2)
C(7)-O(2)	1.380(3)
C(7)-C(7A)	1.415(3)
C(7)-Cr	2.236(3)
C(7A)-C(7B)	1.500(4)
C(7A)-Cr	2.300(3)
C(7B)-C(11A)	1.408(3)
C(7B)-C(8)	1.411(4)
C(8)-C(9)	1.374(4)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.379(4)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.384(4)
C(10)-H(10A)	0.9500
C(11)-C(11A)	1.401(4)
C(11)-H(11A)	0.9500
C(11A)-C(11B)	1.448(4)

C(11B)-Re	2.341(3)
C(12)-Si	1.862(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-Si	1.862(3)
C(13)-H(13C)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13A)	0.9800
C(14)-C(15)	1.539(4)
C(14)-C(17)	1.540(5)
C(14)-C(16)	1.542(4)
C(14)-Si	1.865(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17C)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17A)	0.9800
C(18)-C(19)	1.530(4)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19C)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19A)	0.9800
C(20)-C(21)	1.533(4)
C(20)-H(20A)	0.9900

C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-O(2)	1.451(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(3)	1.138(3)
C(23)-Re	1.930(3)
C(24)-O(4)	1.151(3)
C(24)-Re	1.917(3)
C(25)-O(5)	1.153(3)
C(25)-Re	1.898(3)
C(26)-O(6)	1.159(3)
C(26)-Cr	1.842(3)
C(27)-O(7)	1.157(3)
C(27)-Cr	1.841(3)
C(28)-O(8)	1.162(3)
C(28)-Cr	1.836(3)
O(1)-Si	1.7034(18)
C(29)-C(30)	1.695(14)
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-O(9)	1.496(11)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
O(9)-C(31)	1.470(13)
C(31)-C(32)	1.551(13)

C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(2)-C(1)-C(11B)	106.8(3)
C(2)-C(1)-Re	71.11(16)
C(11B)-C(1)-Re	73.54(16)
C(2)-C(1)-H(1A)	126.6
C(11B)-C(1)-H(1A)	126.6
Re-C(1)-H(1A)	120.6
C(3)-C(2)-C(1)	109.7(3)
C(3)-C(2)-Re	73.48(15)
C(1)-C(2)-Re	72.83(15)
C(3)-C(2)-H(2A)	125.1
C(1)-C(2)-H(2A)	125.1
Re-C(2)-H(2A)	120.2
C(2)-C(3)-C(3A)	107.7(3)
C(2)-C(3)-Re	70.83(14)
C(3A)-C(3)-Re	75.85(13)
C(2)-C(3)-H(3A)	126.2
C(3A)-C(3)-H(3A)	126.2
Re-C(3)-H(3A)	119.0
C(11B)-C(3A)-C(3)	107.1(2)
C(11B)-C(3A)-C(3B)	119.7(3)
C(3)-C(3A)-C(3B)	132.7(3)
C(11B)-C(3A)-Re	70.02(13)
C(3)-C(3A)-Re	68.59(13)
C(3B)-C(3A)-Re	132.34(18)
C(4)-C(3B)-C(7A)	119.4(2)

C(4)-C(3B)-C(3A) 121.3(2)

C(7A)-C(3B)-C(3A) 118.9(2)

C(4)-C(3B)-Cr 73.39(16)

C(7A)-C(3B)-Cr 74.17(16)

C(3A)-C(3B)-Cr 129.64(17)

O(1)-C(4)-C(5) 118.7(2)

O(1)-C(4)-C(3B) 119.0(2)

C(5)-C(4)-C(3B) 122.3(2)

O(1)-C(4)-Cr 133.03(18)

C(5)-C(4)-Cr 70.48(14)

C(3B)-C(4)-Cr 69.58(14)

C(6)-C(5)-C(4) 117.4(2)

C(6)-C(5)-C(18) 121.2(2)

C(4)-C(5)-C(18) 121.3(2)

C(6)-C(5)-Cr 70.27(13)

C(4)-C(5)-Cr 72.88(13)

C(18)-C(5)-Cr 129.25(19)

C(5)-C(6)-C(7) 120.5(2)

C(5)-C(6)-C(20) 120.8(2)

C(7)-C(6)-C(20) 118.2(2)

C(5)-C(6)-Cr 72.58(14)

C(7)-C(6)-Cr 72.19(14)

C(20)-C(6)-Cr 134.47(18)

O(2)-C(7)-C(7A) 122.1(2)

O(2)-C(7)-C(6) 115.0(2)

C(7A)-C(7)-C(6) 122.8(3)

O(2)-C(7)-Cr 132.39(17)

C(7A)-C(7)-Cr 74.31(16)

C(6)-C(7)-Cr 70.42(16)

C(7)-C(7A)-C(3B) 116.8(2)

C(7)-C(7A)-C(7B) 123.8(3)

C(3B)-C(7A)-C(7B) 119.2(2)

C(7)-C(7A)-Cr 69.38(16)

C(3B)-C(7A)-Cr 68.49(16)

C(7B)-C(7A)-Cr 137.31(16)

C(11A)-C(7B)-C(8) 117.0(3)

C(11A)-C(7B)-C(7A) 120.0(2)

C(8)-C(7B)-C(7A) 122.8(2)

C(9)-C(8)-C(7B) 121.3(3)

C(9)-C(8)-H(8A) 119.3

C(7B)-C(8)-H(8A) 119.3

C(8)-C(9)-C(10) 121.6(3)

C(8)-C(9)-H(9A) 119.2

C(10)-C(9)-H(9A) 119.2

C(9)-C(10)-C(11) 118.3(3)

C(9)-C(10)-H(10A) 120.8

C(11)-C(10)-H(10A) 120.8

C(10)-C(11)-C(11A) 121.3(3)

C(10)-C(11)-H(11A) 119.4

C(11A)-C(11)-H(11A) 119.4

C(11)-C(11A)-C(7B) 120.2(3)

C(11)-C(11A)-C(11B) 119.6(3)

C(7B)-C(11A)-C(11B) 120.2(3)

C(3A)-C(11B)-C(1) 108.5(2)

C(3A)-C(11B)-C(11A) 121.3(2)

C(1)-C(11B)-C(11A) 130.2(3)

C(3A)-C(11B)-Re 75.07(15)

C(1)-C(11B)-Re 70.36(15)

C(11A)-C(11B)-Re 122.57(17)

Si-C(12)-H(12A) 109.5

Si-C(12)-H(12B) 109.5

H(12A)-C(12)-H(12B) 109.5

Si-C(12)-H(12C) 109.5

H(12A)-C(12)-H(12C) 109.5

H(12B)-C(12)-H(12C) 109.5

Si-C(13)-H(13C) 109.5

Si-C(13)-H(13B) 109.5

H(13C)-C(13)-H(13B) 109.5

Si-C(13)-H(13A) 109.5

H(13C)-C(13)-H(13A) 109.5

H(13B)-C(13)-H(13A) 109.5

C(15)-C(14)-C(17) 107.8(3)

C(15)-C(14)-C(16) 108.5(3)

C(17)-C(14)-C(16) 109.8(3)

C(15)-C(14)-Si 111.4(2)

C(17)-C(14)-Si 111.3(2)

C(16)-C(14)-Si 108.0(2)

C(14)-C(15)-H(15A) 109.5

C(14)-C(15)-H(15B) 109.5

H(15A)-C(15)-H(15B) 109.5

C(14)-C(15)-H(15C) 109.5

H(15A)-C(15)-H(15C) 109.5

H(15B)-C(15)-H(15C) 109.5

C(14)-C(16)-H(16A) 109.5

C(14)-C(16)-H(16B) 109.5

H(16A)-C(16)-H(16B) 109.5

C(14)-C(16)-H(16C) 109.5

H(16A)-C(16)-H(16C) 109.5

H(16B)-C(16)-H(16C) 109.5

C(14)-C(17)-H(17C) 109.5

C(14)-C(17)-H(17B) 109.5

H(17C)-C(17)-H(17B) 109.5

C(14)-C(17)-H(17A) 109.5

H(17C)-C(17)-H(17A) 109.5

H(17B)-C(17)-H(17A) 109.5

C(5)-C(18)-C(19) 116.6(2)

C(5)-C(18)-H(18A) 108.1

C(19)-C(18)-H(18A) 108.1

C(5)-C(18)-H(18B) 108.1

C(19)-C(18)-H(18B) 108.1

H(18A)-C(18)-H(18B) 107.3

C(18)-C(19)-H(19C) 109.5

C(18)-C(19)-H(19B) 109.5

H(19C)-C(19)-H(19B) 109.5

C(18)-C(19)-H(19A) 109.5

H(19C)-C(19)-H(19A) 109.5

H(19B)-C(19)-H(19A) 109.5

C(6)-C(20)-C(21) 109.3(2)

C(6)-C(20)-H(20A) 109.8

C(21)-C(20)-H(20A) 109.8

C(6)-C(20)-H(20B) 109.8

C(21)-C(20)-H(20B) 109.8

H(20A)-C(20)-H(20B) 108.3

C(20)-C(21)-H(21A) 109.5

C(20)-C(21)-H(21B) 109.5

H(21A)-C(21)-H(21B) 109.5

C(20)-C(21)-H(21C) 109.5

H(21A)-C(21)-H(21C) 109.5

H(21B)-C(21)-H(21C) 109.5

O(2)-C(22)-H(22A) 109.5

O(2)-C(22)-H(22B) 109.5

H(22A)-C(22)-H(22B) 109.5

O(2)-C(22)-H(22C) 109.5

H(22A)-C(22)-H(22C) 109.5

H(22B)-C(22)-H(22C) 109.5

O(3)-C(23)-Re 178.0(3)

O(4)-C(24)-Re 177.2(3)

O(5)-C(25)-Re 178.7(3)

O(6)-C(26)-Cr 176.2(2)

O(7)-C(27)-Cr 179.0(3)

O(8)-C(28)-Cr 178.3(3)

C(28)-Cr-C(27) 87.63(12)

C(28)-Cr-C(26) 89.58(14)

C(27)-Cr-C(26) 91.66(12)

C(28)-Cr-C(6) 87.49(11)

C(27)-Cr-C(6) 139.80(12)

C(26)-Cr-C(6) 128.17(11)

C(28)-Cr-C(3B) 166.52(11)

C(27)-Cr-C(3B) 99.47(11)

C(26)-Cr-C(3B) 101.56(12)

C(6)-Cr-C(3B) 79.69(9)

C(28)-Cr-C(7) 100.83(12)

C(27)-Cr-C(7) 105.16(11)

C(26)-Cr-C(7) 160.44(11)

C(6)-Cr-C(7) 37.39(9)

C(3B)-Cr-C(7) 66.34(10)

C(28)-Cr-C(5) 103.95(10)

C(27)-Cr-C(5) 166.84(12)

C(26)-Cr-C(5) 94.61(11)

C(6)-Cr-C(5) 37.15(9)

C(3B)-Cr-C(5)	67.94(9)
C(7)-Cr-C(5)	66.94(10)
C(28)-Cr-C(4)	138.91(11)
C(27)-Cr-C(4)	133.07(11)
C(26)-Cr-C(4)	84.61(11)
C(6)-Cr-C(4)	65.46(9)
C(3B)-Cr-C(4)	37.04(9)
C(7)-Cr-C(4)	76.64(10)
C(5)-Cr-C(4)	36.64(9)
C(28)-Cr-C(7A)	132.65(12)
C(27)-Cr-C(7A)	87.85(11)
C(26)-Cr-C(7A)	137.66(12)
C(6)-Cr-C(7A)	67.07(9)
C(3B)-Cr-C(7A)	37.34(9)
C(7)-Cr-C(7A)	36.31(9)
C(5)-Cr-C(7A)	79.72(9)
C(4)-Cr-C(7A)	65.86(10)
C(4)-O(1)-Si	124.13(16)
C(7)-O(2)-C(22)	115.7(2)
C(25)-Re-C(24)	87.91(12)
C(25)-Re-C(23)	86.87(14)
C(24)-Re-C(23)	88.57(12)
C(25)-Re-C(2)	94.69(12)
C(24)-Re-C(2)	138.24(12)
C(23)-Re-C(2)	133.16(11)
C(25)-Re-C(1)	106.61(13)
C(24)-Re-C(1)	103.56(11)
C(23)-Re-C(1)	161.95(10)
C(2)-Re-C(1)	36.06(10)
C(25)-Re-C(3)	116.40(11)

C(24)-Re-C(3)	153.05(11)
C(23)-Re-C(3)	103.41(10)
C(2)-Re-C(3)	35.69(9)
C(1)-Re-C(3)	60.10(10)
C(25)-Re-C(11B)	141.99(13)
C(24)-Re-C(11B)	94.40(11)
C(23)-Re-C(11B)	131.07(11)
C(2)-Re-C(11B)	59.50(10)
C(1)-Re-C(11B)	36.10(9)
C(3)-Re-C(11B)	59.49(9)
C(25)-Re-C(3A)	151.41(11)
C(24)-Re-C(3A)	118.52(11)
C(23)-Re-C(3A)	103.40(10)
C(2)-Re-C(3A)	58.76(9)
C(1)-Re-C(3A)	59.14(9)
C(3)-Re-C(3A)	35.56(9)
C(11B)-Re-C(3A)	34.92(9)
O(1)-Si-C(13)	111.54(12)
O(1)-Si-C(12)	110.44(11)
C(13)-Si-C(12)	106.47(15)
O(1)-Si-C(14)	102.75(12)
C(13)-Si-C(14)	112.92(13)
C(12)-Si-C(14)	112.82(16)
C(30)-C(29)-H(29A)	109.5
C(30)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(30)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
O(9)-C(30)-C(29)	91.4(10)

O(9)-C(30)-H(30A)	113.4
C(29)-C(30)-H(30A)	113.4
O(9)-C(30)-H(30B)	113.4
C(29)-C(30)-H(30B)	113.4
H(30A)-C(30)-H(30B)	110.7
C(31)-O(9)-C(30)	109.7(10)
O(9)-C(31)-C(32)	89.4(9)
O(9)-C(31)-H(31A)	113.7
C(32)-C(31)-H(31A)	113.7
O(9)-C(31)-H(31B)	113.7
C(32)-C(31)-H(31B)	113.7
H(31A)-C(31)-H(31B)	111.0
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **25**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	21(1)	20(2)	20(2)	-1(1)	7(1)	-2(1)
C(2)	15(1)	27(2)	15(2)	-1(1)	3(1)	0(1)
C(3)	14(1)	15(2)	16(1)	3(1)	4(1)	3(1)

C(3A)	9(1)	19(2)	15(1)	0(1)	3(1)	-1(1)
C(3B)	12(1)	15(2)	14(1)	-2(1)	4(1)	-5(1)
C(4)	10(1)	16(2)	16(1)	4(1)	2(1)	0(1)
C(5)	12(1)	17(2)	14(1)	0(1)	3(1)	-2(1)
C(6)	13(1)	17(2)	14(1)	0(1)	4(1)	-5(1)
C(7)	11(1)	18(2)	15(1)	1(1)	3(1)	-2(1)
C(7A)	12(1)	15(2)	14(1)	1(1)	4(1)	-3(1)
C(7B)	10(1)	15(2)	19(2)	0(1)	4(1)	-2(1)
C(8)	15(1)	20(2)	18(2)	-3(1)	1(1)	0(1)
C(9)	19(1)	16(2)	25(2)	3(1)	-2(1)	2(1)
C(10)	19(1)	16(2)	29(2)	-6(1)	1(1)	1(1)
C(11)	20(1)	19(2)	20(2)	-4(1)	6(1)	-3(1)
C(11A)	13(1)	15(2)	17(2)	1(1)	4(1)	-1(1)
C(11B)	14(1)	16(2)	15(2)	0(1)	4(1)	-5(1)
C(12)	21(2)	41(2)	39(2)	-11(2)	6(1)	-10(2)
C(13)	20(1)	36(2)	30(2)	6(2)	9(1)	0(1)
C(14)	23(2)	35(2)	25(2)	12(2)	6(1)	8(2)
C(15)	28(2)	39(2)	26(2)	12(2)	2(1)	1(2)
C(16)	19(2)	91(4)	56(3)	44(3)	3(2)	15(2)
C(17)	90(3)	37(3)	37(2)	14(2)	13(2)	36(2)
C(18)	23(1)	25(2)	16(2)	2(1)	6(1)	7(1)
C(19)	36(2)	24(2)	34(2)	-1(2)	15(2)	3(2)
C(20)	16(1)	24(2)	15(1)	0(1)	5(1)	-1(1)
C(21)	25(2)	35(2)	19(2)	2(2)	8(1)	-5(2)
C(22)	18(1)	26(2)	23(2)	1(2)	-5(1)	0(1)
C(23)	20(1)	22(2)	31(2)	2(2)	14(1)	6(1)
C(24)	26(2)	19(2)	23(2)	1(1)	10(1)	-5(1)
C(25)	21(2)	42(2)	27(2)	9(2)	10(1)	5(2)
C(26)	21(1)	21(2)	23(2)	1(2)	11(1)	0(1)
C(27)	19(1)	18(2)	17(2)	1(1)	2(1)	0(1)

C(28)	21(1)	21(2)	22(2)	0(2)	6(1)	-3(1)
Cr	13(1)	16(1)	14(1)	0(1)	4(1)	-1(1)
O(1)	13(1)	19(1)	14(1)	3(1)	2(1)	3(1)
O(2)	16(1)	21(1)	14(1)	5(1)	0(1)	1(1)
O(3)	31(1)	22(1)	50(2)	-4(1)	18(1)	-5(1)
O(4)	19(1)	35(2)	45(2)	5(1)	5(1)	5(1)
O(5)	45(1)	76(2)	29(1)	18(2)	21(1)	5(1)
O(6)	47(1)	24(1)	45(2)	15(1)	25(1)	9(1)
O(7)	15(1)	48(2)	30(1)	2(1)	6(1)	2(1)
O(8)	38(1)	39(2)	26(1)	-8(1)	-1(1)	-8(1)
Re	16(1)	19(1)	15(1)	2(1)	6(1)	1(1)
Si	13(1)	25(1)	18(1)	3(1)	3(1)	2(1)
C(29)	115(11)	114(12)	217(14)	98(11)	85(10)	33(9)
C(30)	52(5)	61(7)	174(11)	-33(7)	-22(6)	28(5)
O(9)	126(7)	107(8)	254(11)	-1(7)	-28(8)	19(7)
C(31)	127(9)	95(9)	216(11)	7(9)	29(8)	17(8)
C(32)	102(7)	74(8)	130(10)	-14(7)	62(7)	-39(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **25**.

	x	y	z	U(eq)
H(1A)	7101	-208	6993	24
H(2A)	5978	1174	6593	22
H(3A)	5718	2140	7532	18
H(8A)	8139	-777	9929	21
H(9A)	9028	-2003	9563	25
H(10A)	9195	-2159	8484	26

H(11A)	8256	-1130	7752	23
H(12A)	2654	955	7614	50
H(12B)	3956	669	7904	50
H(12C)	3734	1339	7310	50
H(13C)	2671	2303	9200	42
H(13B)	3225	1328	9199	42
H(13A)	2009	1540	8757	42
H(15A)	3342	3963	7116	47
H(15B)	3608	2934	7010	47
H(15C)	4498	3518	7494	47
H(16A)	1646	2556	7274	83
H(16B)	1391	3583	7395	83
H(16C)	1276	2863	7939	83
H(17C)	2657	3828	8691	81
H(17B)	2845	4498	8127	81
H(17A)	3944	4022	8540	81
H(18A)	4401	2580	10164	25
H(18B)	4322	3003	9466	25
H(19C)	4945	4055	10292	46
H(19B)	5878	3954	9811	46
H(19A)	6102	3480	10497	46
H(20A)	5918	2193	10921	22
H(20B)	6884	1432	11093	22
H(21A)	5422	319	10867	39
H(21B)	4454	1070	10677	39
H(21C)	5079	977	11403	39
H(22A)	8753	1060	10874	35
H(22B)	9160	484	10311	35
H(22C)	9019	22	10977	35
H(29A)	3036	-672	5003	214

H(29B)	3657	207	5317	214
H(29C)	4187	-751	5524	214
H(30A)	4841	-943	4429	120
H(30B)	4281	22	4208	120
H(31A)	5382	1448	4805	175
H(31B)	5937	897	4259	175
H(32A)	7495	1492	5111	146
H(32B)	7553	434	5034	146
H(32C)	6971	857	5605	146

Table 6. Torsion angles [deg] for **25**.

C(11B)-C(1)-C(2)-C(3)	0.7(3)
Re-C(1)-C(2)-C(3)	-64.72(18)
C(11B)-C(1)-C(2)-Re	65.40(17)
C(1)-C(2)-C(3)-C(3A)	-3.2(3)
Re-C(2)-C(3)-C(3A)	-67.52(17)
C(1)-C(2)-C(3)-Re	64.31(18)
C(2)-C(3)-C(3A)-C(11B)	4.5(3)
Re-C(3)-C(3A)-C(11B)	-59.69(17)
C(2)-C(3)-C(3A)-C(3B)	-167.3(3)
Re-C(3)-C(3A)-C(3B)	128.5(3)
C(2)-C(3)-C(3A)-Re	64.17(17)
C(11B)-C(3A)-C(3B)-C(4)	-163.3(2)
C(3)-C(3A)-C(3B)-C(4)	7.7(4)
Re-C(3A)-C(3B)-C(4)	107.4(3)
C(11B)-C(3A)-C(3B)-C(7A)	9.7(3)
C(3)-C(3A)-C(3B)-C(7A)	-179.3(3)
Re-C(3A)-C(3B)-C(7A)	-79.6(3)

C(11B)-C(3A)-C(3B)-Cr	102.8(3)
C(3)-C(3A)-C(3B)-Cr	-86.3(3)
Re-C(3A)-C(3B)-Cr	13.5(4)
C(7A)-C(3B)-C(4)-O(1)	-170.9(2)
C(3A)-C(3B)-C(4)-O(1)	2.1(4)
Cr-C(3B)-C(4)-O(1)	128.8(2)
C(7A)-C(3B)-C(4)-C(5)	11.4(4)
C(3A)-C(3B)-C(4)-C(5)	-175.6(2)
Cr-C(3B)-C(4)-C(5)	-48.9(2)
C(7A)-C(3B)-C(4)-Cr	60.3(2)
C(3A)-C(3B)-C(4)-Cr	-126.7(2)
O(1)-C(4)-C(5)-C(6)	174.7(2)
C(3B)-C(4)-C(5)-C(6)	-7.6(4)
Cr-C(4)-C(5)-C(6)	-56.1(2)
O(1)-C(4)-C(5)-C(18)	-3.2(4)
C(3B)-C(4)-C(5)-C(18)	174.5(2)
Cr-C(4)-C(5)-C(18)	126.0(3)
O(1)-C(4)-C(5)-Cr	-129.1(2)
C(3B)-C(4)-C(5)-Cr	48.5(2)
C(4)-C(5)-C(6)-C(7)	1.2(4)
C(18)-C(5)-C(6)-C(7)	179.2(2)
Cr-C(5)-C(6)-C(7)	-56.2(2)
C(4)-C(5)-C(6)-C(20)	-170.7(2)
C(18)-C(5)-C(6)-C(20)	7.2(4)
Cr-C(5)-C(6)-C(20)	131.9(2)
C(4)-C(5)-C(6)-Cr	57.4(2)
C(18)-C(5)-C(6)-Cr	-124.7(2)
C(5)-C(6)-C(7)-O(2)	-175.0(2)
C(20)-C(6)-C(7)-O(2)	-2.9(3)
Cr-C(6)-C(7)-O(2)	128.6(2)

C(5)-C(6)-C(7)-C(7A)	1.2(4)
C(20)-C(6)-C(7)-C(7A)	173.3(2)
Cr-C(6)-C(7)-C(7A)	-55.2(2)
C(5)-C(6)-C(7)-Cr	56.4(2)
C(20)-C(6)-C(7)-Cr	-131.5(2)
O(2)-C(7)-C(7A)-C(3B)	178.4(2)
C(6)-C(7)-C(7A)-C(3B)	2.5(4)
Cr-C(7)-C(7A)-C(3B)	-51.0(2)
O(2)-C(7)-C(7A)-C(7B)	3.3(4)
C(6)-C(7)-C(7A)-C(7B)	-172.6(2)
Cr-C(7)-C(7A)-C(7B)	133.9(2)
O(2)-C(7)-C(7A)-Cr	-130.6(2)
C(6)-C(7)-C(7A)-Cr	53.5(2)
C(4)-C(3B)-C(7A)-C(7)	-8.5(4)
C(3A)-C(3B)-C(7A)-C(7)	178.4(2)
Cr-C(3B)-C(7A)-C(7)	51.5(2)
C(4)-C(3B)-C(7A)-C(7B)	166.9(2)
C(3A)-C(3B)-C(7A)-C(7B)	-6.3(3)
Cr-C(3B)-C(7A)-C(7B)	-133.2(2)
C(4)-C(3B)-C(7A)-Cr	-59.9(2)
C(3A)-C(3B)-C(7A)-Cr	126.9(2)
C(7)-C(7A)-C(7B)-C(11A)	176.9(2)
C(3B)-C(7A)-C(7B)-C(11A)	1.9(3)
Cr-C(7A)-C(7B)-C(11A)	-87.3(3)
C(7)-C(7A)-C(7B)-C(8)	2.7(4)
C(3B)-C(7A)-C(7B)-C(8)	-172.3(2)
Cr-C(7A)-C(7B)-C(8)	98.5(3)
C(11A)-C(7B)-C(8)-C(9)	4.3(4)
C(7A)-C(7B)-C(8)-C(9)	178.7(2)
C(7B)-C(8)-C(9)-C(10)	0.2(4)

C(8)-C(9)-C(10)-C(11)	-4.0(4)
C(9)-C(10)-C(11)-C(11A)	3.1(4)
C(10)-C(11)-C(11A)-C(7B)	1.5(4)
C(10)-C(11)-C(11A)-C(11B)	-177.3(2)
C(8)-C(7B)-C(11A)-C(11)	-5.1(4)
C(7A)-C(7B)-C(11A)-C(11)	-179.7(2)
C(8)-C(7B)-C(11A)-C(11B)	173.7(2)
C(7A)-C(7B)-C(11A)-C(11B)	-0.8(4)
C(3)-C(3A)-C(11B)-C(1)	-4.1(3)
C(3B)-C(3A)-C(11B)-C(1)	169.0(2)
Re-C(3A)-C(11B)-C(1)	-62.88(17)
C(3)-C(3A)-C(11B)-C(11A)	178.1(2)
C(3B)-C(3A)-C(11B)-C(11A)	-8.8(4)
Re-C(3A)-C(11B)-C(11A)	119.3(2)
C(3)-C(3A)-C(11B)-Re	58.79(17)
C(3B)-C(3A)-C(11B)-Re	-128.1(2)
C(2)-C(1)-C(11B)-C(3A)	2.2(3)
Re-C(1)-C(11B)-C(3A)	65.94(18)
C(2)-C(1)-C(11B)-C(11A)	179.7(2)
Re-C(1)-C(11B)-C(11A)	-116.5(3)
C(2)-C(1)-C(11B)-Re	-63.77(18)
C(11)-C(11A)-C(11B)-C(3A)	-176.8(2)
C(7B)-C(11A)-C(11B)-C(3A)	4.4(4)
C(11)-C(11A)-C(11B)-C(1)	5.9(4)
C(7B)-C(11A)-C(11B)-C(1)	-172.9(2)
C(11)-C(11A)-C(11B)-Re	-85.1(3)
C(7B)-C(11A)-C(11B)-Re	96.1(3)
C(6)-C(5)-C(18)-C(19)	74.7(3)
C(4)-C(5)-C(18)-C(19)	-107.5(3)
Cr-C(5)-C(18)-C(19)	-14.5(4)

C(5)-C(6)-C(20)-C(21)	90.8(3)
C(7)-C(6)-C(20)-C(21)	-81.3(3)
Cr-C(6)-C(20)-C(21)	-173.6(2)
O(8)-C(28)-Cr-C(27)	-101(8)
O(8)-C(28)-Cr-C(26)	168(8)
O(8)-C(28)-Cr-C(6)	39(8)
O(8)-C(28)-Cr-C(3B)	22(9)
O(8)-C(28)-Cr-C(7)	4(8)
O(8)-C(28)-Cr-C(5)	73(8)
O(8)-C(28)-Cr-C(4)	86(8)
O(8)-C(28)-Cr-C(7A)	-16(8)
O(7)-C(27)-Cr-C(28)	85(16)
O(7)-C(27)-Cr-C(26)	175(100)
O(7)-C(27)-Cr-C(6)	2(17)
O(7)-C(27)-Cr-C(3B)	-83(16)
O(7)-C(27)-Cr-C(7)	-15(16)
O(7)-C(27)-Cr-C(5)	-67(17)
O(7)-C(27)-Cr-C(4)	-101(16)
O(7)-C(27)-Cr-C(7A)	-47(16)
O(6)-C(26)-Cr-C(28)	-107(4)
O(6)-C(26)-Cr-C(27)	165(4)
O(6)-C(26)-Cr-C(6)	-21(4)
O(6)-C(26)-Cr-C(3B)	65(4)
O(6)-C(26)-Cr-C(7)	16(5)
O(6)-C(26)-Cr-C(5)	-3(4)
O(6)-C(26)-Cr-C(4)	32(4)
O(6)-C(26)-Cr-C(7A)	77(4)
C(5)-C(6)-Cr-C(28)	117.24(18)
C(7)-C(6)-Cr-C(28)	-111.55(17)
C(20)-C(6)-Cr-C(28)	0.9(3)

C(5)-C(6)-Cr-C(27)	-159.43(19)
C(7)-C(6)-Cr-C(27)	-28.2(3)
C(20)-C(6)-Cr-C(27)	84.2(3)
C(5)-C(6)-Cr-C(26)	29.7(2)
C(7)-C(6)-Cr-C(26)	160.96(17)
C(20)-C(6)-Cr-C(26)	-86.6(3)
C(5)-C(6)-Cr-C(3B)	-66.92(17)
C(7)-C(6)-Cr-C(3B)	64.29(16)
C(20)-C(6)-Cr-C(3B)	176.7(3)
C(5)-C(6)-Cr-C(7)	-131.2(2)
C(20)-C(6)-Cr-C(7)	112.4(3)
C(7)-C(6)-Cr-C(5)	131.2(2)
C(20)-C(6)-Cr-C(5)	-116.4(3)
C(5)-C(6)-Cr-C(4)	-30.91(16)
C(7)-C(6)-Cr-C(4)	100.31(17)
C(20)-C(6)-Cr-C(4)	-147.3(3)
C(5)-C(6)-Cr-C(7A)	-103.75(18)
C(7)-C(6)-Cr-C(7A)	27.47(15)
C(20)-C(6)-Cr-C(7A)	139.9(3)
C(4)-C(3B)-Cr-C(28)	80.7(5)
C(7A)-C(3B)-Cr-C(28)	-47.4(5)
C(3A)-C(3B)-Cr-C(28)	-162.1(4)
C(4)-C(3B)-Cr-C(27)	-158.19(17)
C(7A)-C(3B)-Cr-C(27)	73.66(16)
C(3A)-C(3B)-Cr-C(27)	-41.0(3)
C(4)-C(3B)-Cr-C(26)	-64.52(17)
C(7A)-C(3B)-Cr-C(26)	167.34(14)
C(3A)-C(3B)-Cr-C(26)	52.6(3)
C(4)-C(3B)-Cr-C(6)	62.63(16)
C(7A)-C(3B)-Cr-C(6)	-65.52(14)

C(3A)-C(3B)-Cr-C(6)	179.8(3)
C(4)-C(3B)-Cr-C(7)	99.31(16)
C(7A)-C(3B)-Cr-C(7)	-28.84(13)
C(3A)-C(3B)-Cr-C(7)	-143.5(3)
C(4)-C(3B)-Cr-C(5)	25.80(15)
C(7A)-C(3B)-Cr-C(5)	-102.34(15)
C(3A)-C(3B)-Cr-C(5)	143.0(3)
C(7A)-C(3B)-Cr-C(4)	-128.1(2)
C(3A)-C(3B)-Cr-C(4)	117.1(3)
C(4)-C(3B)-Cr-C(7A)	128.1(2)
C(3A)-C(3B)-Cr-C(7A)	-114.7(3)
O(2)-C(7)-Cr-C(28)	-35.4(3)
C(7A)-C(7)-Cr-C(28)	-154.73(15)
C(6)-C(7)-Cr-C(28)	71.10(17)
O(2)-C(7)-Cr-C(27)	55.1(3)
C(7A)-C(7)-Cr-C(27)	-64.26(17)
C(6)-C(7)-Cr-C(27)	161.57(17)
O(2)-C(7)-Cr-C(26)	-156.5(3)
C(7A)-C(7)-Cr-C(26)	84.2(4)
C(6)-C(7)-Cr-C(26)	-50.0(4)
O(2)-C(7)-Cr-C(6)	-106.5(3)
C(7A)-C(7)-Cr-C(6)	134.2(2)
O(2)-C(7)-Cr-C(3B)	149.0(3)
C(7A)-C(7)-Cr-C(3B)	29.60(14)
C(6)-C(7)-Cr-C(3B)	-104.57(17)
O(2)-C(7)-Cr-C(5)	-136.1(3)
C(7A)-C(7)-Cr-C(5)	104.59(16)
C(6)-C(7)-Cr-C(5)	-29.59(15)
O(2)-C(7)-Cr-C(4)	-173.4(3)
C(7A)-C(7)-Cr-C(4)	67.26(15)

C(6)-C(7)-Cr-C(4)	-66.91(16)
O(2)-C(7)-Cr-C(7A)	119.4(3)
C(6)-C(7)-Cr-C(7A)	-134.2(2)
C(6)-C(5)-Cr-C(28)	-66.24(19)
C(4)-C(5)-Cr-C(28)	165.28(18)
C(18)-C(5)-Cr-C(28)	48.5(3)
C(6)-C(5)-Cr-C(27)	84.9(5)
C(4)-C(5)-Cr-C(27)	-43.6(6)
C(18)-C(5)-Cr-C(27)	-160.4(4)
C(6)-C(5)-Cr-C(26)	-156.96(18)
C(4)-C(5)-Cr-C(26)	74.56(19)
C(18)-C(5)-Cr-C(26)	-42.2(3)
C(4)-C(5)-Cr-C(6)	-128.5(3)
C(18)-C(5)-Cr-C(6)	114.7(3)
C(6)-C(5)-Cr-C(3B)	102.42(18)
C(4)-C(5)-Cr-C(3B)	-26.06(17)
C(18)-C(5)-Cr-C(3B)	-142.8(3)
C(6)-C(5)-Cr-C(7)	29.77(16)
C(4)-C(5)-Cr-C(7)	-98.71(18)
C(18)-C(5)-Cr-C(7)	144.5(3)
C(6)-C(5)-Cr-C(4)	128.5(3)
C(18)-C(5)-Cr-C(4)	-116.8(3)
C(6)-C(5)-Cr-C(7A)	65.39(17)
C(4)-C(5)-Cr-C(7A)	-63.09(17)
C(18)-C(5)-Cr-C(7A)	-179.9(3)
O(1)-C(4)-Cr-C(28)	89.4(3)
C(5)-C(4)-Cr-C(28)	-22.0(3)
C(3B)-C(4)-Cr-C(28)	-159.51(19)
O(1)-C(4)-Cr-C(27)	-81.0(3)
C(5)-C(4)-Cr-C(27)	167.58(19)

C(3B)-C(4)-Cr-C(27)	30.1(2)
O(1)-C(4)-Cr-C(26)	6.3(2)
C(5)-C(4)-Cr-C(26)	-105.19(18)
C(3B)-C(4)-Cr-C(26)	117.34(17)
O(1)-C(4)-Cr-C(6)	142.8(3)
C(5)-C(4)-Cr-C(6)	31.31(17)
C(3B)-C(4)-Cr-C(6)	-106.16(18)
O(1)-C(4)-Cr-C(3B)	-111.1(3)
C(5)-C(4)-Cr-C(3B)	137.5(2)
O(1)-C(4)-Cr-C(7)	-179.4(3)
C(5)-C(4)-Cr-C(7)	69.19(17)
C(3B)-C(4)-Cr-C(7)	-68.28(16)
O(1)-C(4)-Cr-C(5)	111.4(3)
C(3B)-C(4)-Cr-C(5)	-137.5(2)
O(1)-C(4)-Cr-C(7A)	-142.6(3)
C(5)-C(4)-Cr-C(7A)	105.96(18)
C(3B)-C(4)-Cr-C(7A)	-31.52(15)
C(7)-C(7A)-Cr-C(28)	34.7(2)
C(3B)-C(7A)-Cr-C(28)	166.51(15)
C(7B)-C(7A)-Cr-C(28)	-83.2(3)
C(7)-C(7A)-Cr-C(27)	119.54(16)
C(3B)-C(7A)-Cr-C(27)	-108.70(15)
C(7B)-C(7A)-Cr-C(27)	1.6(3)
C(7)-C(7A)-Cr-C(26)	-150.36(17)
C(3B)-C(7A)-Cr-C(26)	-18.6(2)
C(7B)-C(7A)-Cr-C(26)	91.7(3)
C(7)-C(7A)-Cr-C(6)	-28.22(14)
C(3B)-C(7A)-Cr-C(6)	103.54(15)
C(7B)-C(7A)-Cr-C(6)	-146.2(3)
C(7)-C(7A)-Cr-C(3B)	-131.8(2)

C(7B)-C(7A)-Cr-C(3B)	110.3(3)
C(3B)-C(7A)-Cr-C(7)	131.8(2)
C(7B)-C(7A)-Cr-C(7)	-117.9(3)
C(7)-C(7A)-Cr-C(5)	-64.82(15)
C(3B)-C(7A)-Cr-C(5)	66.94(14)
C(7B)-C(7A)-Cr-C(5)	177.3(3)
C(7)-C(7A)-Cr-C(4)	-100.49(15)
C(3B)-C(7A)-Cr-C(4)	31.27(13)
C(7B)-C(7A)-Cr-C(4)	141.6(3)
C(5)-C(4)-O(1)-Si	-83.9(3)
C(3B)-C(4)-O(1)-Si	98.3(2)
Cr-C(4)-O(1)-Si	-173.30(13)
C(7A)-C(7)-O(2)-C(22)	85.6(3)
C(6)-C(7)-O(2)-C(22)	-98.2(3)
Cr-C(7)-O(2)-C(22)	-12.4(3)
O(5)-C(25)-Re-C(24)	109(13)
O(5)-C(25)-Re-C(23)	-162(13)
O(5)-C(25)-Re-C(2)	-29(13)
O(5)-C(25)-Re-C(1)	6(13)
O(5)-C(25)-Re-C(3)	-59(13)
O(5)-C(25)-Re-C(11B)	15(13)
O(5)-C(25)-Re-C(3A)	-50(13)
O(4)-C(24)-Re-C(25)	-121(5)
O(4)-C(24)-Re-C(23)	152(5)
O(4)-C(24)-Re-C(2)	-26(5)
O(4)-C(24)-Re-C(1)	-15(5)
O(4)-C(24)-Re-C(3)	34(5)
O(4)-C(24)-Re-C(11B)	21(5)
O(4)-C(24)-Re-C(3A)	47(5)
O(3)-C(23)-Re-C(25)	-6(8)

O(3)-C(23)-Re-C(24)	82(8)
O(3)-C(23)-Re-C(2)	-99(8)
O(3)-C(23)-Re-C(1)	-145(8)
O(3)-C(23)-Re-C(3)	-122(8)
O(3)-C(23)-Re-C(11B)	177(100)
O(3)-C(23)-Re-C(3A)	-159(8)
C(3)-C(2)-Re-C(25)	-130.59(19)
C(1)-C(2)-Re-C(25)	112.01(18)
C(3)-C(2)-Re-C(24)	137.30(18)
C(1)-C(2)-Re-C(24)	19.9(2)
C(3)-C(2)-Re-C(23)	-40.5(2)
C(1)-C(2)-Re-C(23)	-157.89(17)
C(3)-C(2)-Re-C(1)	117.4(2)
C(1)-C(2)-Re-C(3)	-117.4(2)
C(3)-C(2)-Re-C(11B)	79.05(18)
C(1)-C(2)-Re-C(11B)	-38.36(15)
C(3)-C(2)-Re-C(3A)	38.14(16)
C(1)-C(2)-Re-C(3A)	-79.27(17)
C(2)-C(1)-Re-C(25)	-74.64(17)
C(11B)-C(1)-Re-C(25)	170.52(16)
C(2)-C(1)-Re-C(24)	-166.52(15)
C(11B)-C(1)-Re-C(24)	78.64(17)
C(2)-C(1)-Re-C(23)	62.4(4)
C(11B)-C(1)-Re-C(23)	-52.5(4)
C(11B)-C(1)-Re-C(2)	-114.8(2)
C(2)-C(1)-Re-C(3)	36.69(15)
C(11B)-C(1)-Re-C(3)	-78.15(16)
C(2)-C(1)-Re-C(11B)	114.8(2)
C(2)-C(1)-Re-C(3A)	78.14(16)
C(11B)-C(1)-Re-C(3A)	-36.70(14)

C(2)-C(3)-Re-C(25)	57.7(2)
C(3A)-C(3)-Re-C(25)	172.44(19)
C(2)-C(3)-Re-C(24)	-94.8(3)
C(3A)-C(3)-Re-C(24)	20.0(3)
C(2)-C(3)-Re-C(23)	150.87(19)
C(3A)-C(3)-Re-C(23)	-94.36(18)
C(3A)-C(3)-Re-C(2)	114.8(3)
C(2)-C(3)-Re-C(1)	-37.07(17)
C(3A)-C(3)-Re-C(1)	77.70(18)
C(2)-C(3)-Re-C(11B)	-79.08(18)
C(3A)-C(3)-Re-C(11B)	35.68(16)
C(2)-C(3)-Re-C(3A)	-114.8(3)
C(3A)-C(11B)-Re-C(25)	-131.17(19)
C(1)-C(11B)-Re-C(25)	-14.8(3)
C(11A)-C(11B)-Re-C(25)	111.0(3)
C(3A)-C(11B)-Re-C(24)	136.59(17)
C(1)-C(11B)-Re-C(24)	-107.08(17)
C(11A)-C(11B)-Re-C(24)	18.7(2)
C(3A)-C(11B)-Re-C(23)	44.7(2)
C(1)-C(11B)-Re-C(23)	160.98(17)
C(11A)-C(11B)-Re-C(23)	-73.2(3)
C(3A)-C(11B)-Re-C(2)	-78.02(17)
C(1)-C(11B)-Re-C(2)	38.31(15)
C(11A)-C(11B)-Re-C(2)	164.1(3)
C(3A)-C(11B)-Re-C(1)	-116.3(2)
C(11A)-C(11B)-Re-C(1)	125.8(3)
C(3A)-C(11B)-Re-C(3)	-36.35(15)
C(1)-C(11B)-Re-C(3)	79.98(17)
C(11A)-C(11B)-Re-C(3)	-154.2(3)
C(1)-C(11B)-Re-C(3A)	116.3(2)

C(11A)-C(11B)-Re-C(3A)	-117.9(3)
C(11B)-C(3A)-Re-C(25)	104.3(3)
C(3)-C(3A)-Re-C(25)	-14.3(3)
C(3B)-C(3A)-Re-C(25)	-143.2(3)
C(11B)-C(3A)-Re-C(24)	-51.2(2)
C(3)-C(3A)-Re-C(24)	-169.84(17)
C(3B)-C(3A)-Re-C(24)	61.2(3)
C(11B)-C(3A)-Re-C(23)	-147.00(17)
C(3)-C(3A)-Re-C(23)	94.40(18)
C(3B)-C(3A)-Re-C(23)	-34.6(3)
C(11B)-C(3A)-Re-C(2)	80.32(17)
C(3)-C(3A)-Re-C(2)	-38.28(17)
C(3B)-C(3A)-Re-C(2)	-167.2(3)
C(11B)-C(3A)-Re-C(1)	37.97(16)
C(3)-C(3A)-Re-C(1)	-80.63(18)
C(3B)-C(3A)-Re-C(1)	150.4(3)
C(11B)-C(3A)-Re-C(3)	118.6(2)
C(3B)-C(3A)-Re-C(3)	-129.0(4)
C(3)-C(3A)-Re-C(11B)	-118.6(2)
C(3B)-C(3A)-Re-C(11B)	112.4(3)
C(4)-O(1)-Si-C(13)	41.3(2)
C(4)-O(1)-Si-C(12)	-76.9(2)
C(4)-O(1)-Si-C(14)	162.5(2)
C(15)-C(14)-Si-O(1)	60.3(2)
C(17)-C(14)-Si-O(1)	-60.1(2)
C(16)-C(14)-Si-O(1)	179.3(2)
C(15)-C(14)-Si-C(13)	-179.4(2)
C(17)-C(14)-Si-C(13)	60.2(3)
C(16)-C(14)-Si-C(13)	-60.4(3)
C(15)-C(14)-Si-C(12)	-58.6(3)

C(17)-C(14)-Si-C(12)	-179.0(2)
C(16)-C(14)-Si-C(12)	60.4(2)
C(29)-C(30)-O(9)-C(31)	-124.4(11)
C(30)-O(9)-C(31)-C(32)	-159.8(10)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **25** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.12 Pentacarbonyl[4-benzo[*h*]quinolyl(-methoxy)carbene]chromium(0) (29)

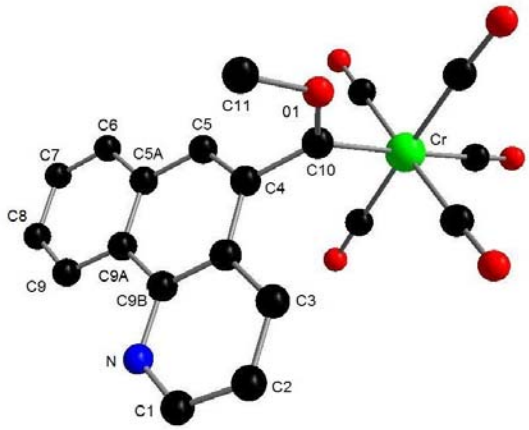


Table 1. Crystal data and structure refinement for **29**.

Formula weight	413.30
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 6.6296(4) A alpha = 90 deg.
	b = 11.1970(9) A beta = 90.670(4) deg.
	c = 23.8845(18) A gamma = 90 deg.
Volume	1772.9(2) A^3
Z, Calculated density	4, 1.548 Mg/m^3

Absorption coefficient	0.684 mm^-1
F(000)	840
Crystal size	0.48 x 0.08 x 0.04 mm
Theta range for data collection	2.01 to 27.50 deg.
Limiting indices	-8<=h<=7, -13<=k<=14, -31<=l<=21
Reflections collected / unique	9732 / 4039 [R(int) = 0.0781]
Completeness to theta = 27.50	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.95170 and 0.81388
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4039 / 0 / 253
Goodness-of-fit on F^2	0.942
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1103
R indices (all data)	R1 = 0.1181, wR2 = 0.1297
Largest diff. peak and hole	0.360 and -0.608 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **29**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8697(5)	893(3)	2447(2)	30(1)
C(2)	9378(5)	1060(3)	1902(2)	30(1)
C(3)	8306(5)	1787(3)	1547(2)	27(1)
C(3A)	6517(5)	2328(3)	1743(2)	22(1)
C(4)	5287(5)	3102(3)	1392(2)	22(1)
C(5)	3602(5)	3620(3)	1607(2)	24(1)
C(5A)	3006(5)	3428(3)	2172(2)	23(1)
C(6)	1306(5)	4025(3)	2398(2)	28(1)

C(7)	761(5)	3843(3)	2936(2)	30(1)
C(8)	1884(6)	3063(4)	3280(2)	36(1)
C(9)	3543(5)	2496(3)	3075(2)	30(1)
C(9A)	4142(5)	2665(3)	2522(2)	24(1)
C(9B)	5947(5)	2115(3)	2294(2)	23(1)
C(10)	5800(5)	3315(3)	791(2)	24(1)
C(11)	7788(5)	4994(4)	1156(2)	32(1)
C(12)	3607(5)	1509(3)	-474(2)	27(1)
C(13)	5976(5)	3477(3)	-347(2)	25(1)
C(14)	7265(5)	1547(3)	100(2)	26(1)
C(15)	3663(5)	1227(3)	638(2)	26(1)
C(16)	2332(5)	3262(4)	170(2)	28(1)
Cr	4764(1)	2371(1)	139(1)	23(1)
N	7030(4)	1388(3)	2644(1)	28(1)
O(1)	7006(3)	4240(2)	699(1)	28(1)
O(2)	2876(4)	1025(3)	-845(1)	38(1)
O(3)	6749(4)	4107(2)	-660(1)	33(1)
O(4)	8825(4)	1106(2)	72(1)	38(1)
O(5)	2968(4)	527(3)	929(1)	37(1)
O(6)	843(4)	3783(2)	190(1)	40(1)

Table 3. Bond lengths [A] and angles [deg] for **29**.

C(1)-N	1.327(4)
C(1)-C(2)	1.395(5)
C(1)-H(1)	0.9500
C(2)-C(3)	1.369(5)
C(2)-H(2)	0.9500
C(3)-C(3A)	1.416(5)

C(3)-H(3)	0.9500
C(3A)-C(9B)	1.393(5)
C(3A)-C(4)	1.450(5)
C(4)-C(5)	1.364(5)
C(4)-C(10)	1.499(5)
C(5)-C(5A)	1.427(5)
C(5)-H(5)	0.9500
C(5A)-C(9A)	1.408(5)
C(5A)-C(6)	1.422(5)
C(6)-C(7)	1.354(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.407(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.365(5)
C(8)-H(8)	0.9500
C(9)-C(9A)	1.396(5)
C(9)-H(9)	0.9500
C(9A)-C(9B)	1.458(5)
C(9B)-N	1.365(4)
C(10)-O(1)	1.328(4)
C(10)-Cr	1.998(4)
C(11)-O(1)	1.469(4)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-O(2)	1.141(4)
C(12)-Cr	1.907(4)
C(13)-O(3)	1.153(4)
C(13)-Cr	1.884(4)
C(14)-O(4)	1.149(4)

C(14)-Cr	1.900(4)
C(15)-O(5)	1.148(4)
C(15)-Cr	1.900(4)
C(16)-O(6)	1.148(4)
C(16)-Cr	1.898(4)
N-C(1)-C(2)	123.6(4)
N-C(1)-H(1)	118.2
C(2)-C(1)-H(1)	118.2
C(3)-C(2)-C(1)	119.1(4)
C(3)-C(2)-H(2)	120.5
C(1)-C(2)-H(2)	120.5
C(2)-C(3)-C(3A)	118.7(4)
C(2)-C(3)-H(3)	120.6
C(3A)-C(3)-H(3)	120.6
C(9B)-C(3A)-C(3)	118.4(3)
C(9B)-C(3A)-C(4)	119.4(3)
C(3)-C(3A)-C(4)	122.1(3)
C(5)-C(4)-C(3A)	119.6(3)
C(5)-C(4)-C(10)	119.2(3)
C(3A)-C(4)-C(10)	121.1(3)
C(4)-C(5)-C(5A)	121.9(3)
C(4)-C(5)-H(5)	119.1
C(5A)-C(5)-H(5)	119.1
C(9A)-C(5A)-C(6)	118.8(3)
C(9A)-C(5A)-C(5)	120.1(3)
C(6)-C(5A)-C(5)	121.1(3)
C(7)-C(6)-C(5A)	120.7(4)
C(7)-C(6)-H(6)	119.7
C(5A)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	120.1(4)

C(6)-C(7)-H(7) 119.9

C(8)-C(7)-H(7) 119.9

C(9)-C(8)-C(7) 120.2(4)

C(9)-C(8)-H(8) 119.9

C(7)-C(8)-H(8) 119.9

C(8)-C(9)-C(9A) 121.0(4)

C(8)-C(9)-H(9) 119.5

C(9A)-C(9)-H(9) 119.5

C(9)-C(9A)-C(5A) 119.2(3)

C(9)-C(9A)-C(9B) 122.7(3)

C(5A)-C(9A)-C(9B) 118.0(3)

N-C(9B)-C(3A) 122.3(3)

N-C(9B)-C(9A) 116.8(3)

C(3A)-C(9B)-C(9A) 120.9(3)

O(1)-C(10)-C(4) 115.2(3)

O(1)-C(10)-Cr 119.1(3)

C(4)-C(10)-Cr 125.6(3)

O(1)-C(11)-H(11A) 109.5

O(1)-C(11)-H(11B) 109.5

H(11A)-C(11)-H(11B) 109.5

O(1)-C(11)-H(11C) 109.5

H(11A)-C(11)-H(11C) 109.5

H(11B)-C(11)-H(11C) 109.5

O(2)-C(12)-Cr 177.8(3)

O(3)-C(13)-Cr 176.6(3)

O(4)-C(14)-Cr 176.4(3)

O(5)-C(15)-Cr 178.4(3)

O(6)-C(16)-Cr 178.8(3)

C(13)-Cr-C(16) 92.72(15)

C(13)-Cr-C(15) 177.31(15)

C(16)-Cr-C(15)	89.83(15)
C(13)-Cr-C(14)	84.85(16)
C(16)-Cr-C(14)	177.27(16)
C(15)-Cr-C(14)	92.58(15)
C(13)-Cr-C(12)	91.71(16)
C(16)-Cr-C(12)	87.84(16)
C(15)-Cr-C(12)	89.26(16)
C(14)-Cr-C(12)	93.45(15)
C(13)-Cr-C(10)	89.24(16)
C(16)-Cr-C(10)	88.58(15)
C(15)-Cr-C(10)	89.95(16)
C(14)-Cr-C(10)	90.15(15)
C(12)-Cr-C(10)	176.34(14)
C(1)-N-C(9B)	117.8(3)
C(10)-O(1)-C(11)	122.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **29**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	27(2)	31(2)	32(3)	3(2)	-5(2)	5(2)
C(2)	25(2)	31(2)	35(3)	5(2)	1(2)	10(2)
C(3)	21(2)	31(2)	29(2)	2(2)	1(2)	1(2)
C(3A)	20(2)	24(2)	22(2)	-1(2)	-3(1)	0(2)
C(4)	21(2)	25(2)	22(2)	0(2)	-3(2)	-3(2)
C(5)	18(2)	31(2)	24(2)	2(2)	-4(2)	0(2)

C(5A)	19(2)	25(2)	24(2)	0(2)	-2(1)	-1(2)
C(6)	20(2)	33(2)	31(2)	1(2)	-3(2)	2(2)
C(7)	26(2)	35(2)	29(2)	-3(2)	4(2)	5(2)
C(8)	38(2)	41(3)	28(2)	6(2)	9(2)	7(2)
C(9)	28(2)	31(2)	31(2)	6(2)	0(2)	6(2)
C(9A)	22(2)	24(2)	25(2)	1(2)	-1(1)	0(2)
C(9B)	20(2)	22(2)	25(2)	1(2)	-2(2)	0(2)
C(10)	12(2)	28(2)	33(2)	3(2)	-5(2)	6(2)
C(11)	26(2)	41(2)	28(3)	-8(2)	-6(2)	-14(2)
C(12)	27(2)	25(2)	28(2)	0(2)	5(2)	0(2)
C(13)	25(2)	31(2)	21(2)	-5(2)	-2(2)	6(2)
C(14)	28(2)	25(2)	26(2)	-3(2)	1(2)	-4(2)
C(15)	23(2)	30(2)	27(2)	0(2)	-1(2)	5(2)
C(16)	25(2)	32(2)	27(2)	0(2)	-1(2)	-5(2)
Cr	18(1)	26(1)	24(1)	0(1)	-1(1)	1(1)
N	24(2)	31(2)	30(2)	5(2)	-3(1)	4(1)
O(1)	22(1)	35(2)	28(2)	-3(1)	-2(1)	-10(1)
O(2)	38(2)	45(2)	32(2)	-12(2)	-2(1)	-12(1)
O(3)	36(2)	33(2)	28(2)	6(1)	-1(1)	-5(1)
O(4)	25(1)	36(2)	53(2)	-5(2)	5(1)	6(1)
O(5)	38(2)	37(2)	37(2)	8(2)	6(1)	-5(1)
O(6)	21(1)	42(2)	57(2)	-5(2)	-3(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **29**.

	x	y	z	U(eq)
H(1)	9470	397	2691	36

H(2)	10569	674	1779	36
H(3)	8753	1927	1177	33
H(5)	2802	4124	1374	29
H(6)	545	4557	2169	33
H(7)	-383	4244	3081	36
H(8)	1487	2929	3655	43
H(9)	4302	1980	3313	36
H(11A)	8586	4504	1417	48
H(11B)	6659	5357	1355	48
H(11C)	8643	5624	1001	48

Table 6. Torsion angles [deg] for **29**.

N-C(1)-C(2)-C(3)	1.2(6)
C(1)-C(2)-C(3)-C(3A)	-1.2(6)
C(2)-C(3)-C(3A)-C(9B)	1.3(5)
C(2)-C(3)-C(3A)-C(4)	-179.5(3)
C(9B)-C(3A)-C(4)-C(5)	0.7(5)
C(3)-C(3A)-C(4)-C(5)	-178.5(3)
C(9B)-C(3A)-C(4)-C(10)	-177.5(3)
C(3)-C(3A)-C(4)-C(10)	3.3(5)
C(3A)-C(4)-C(5)-C(5A)	0.2(5)
C(10)-C(4)-C(5)-C(5A)	178.4(3)
C(4)-C(5)-C(5A)-C(9A)	-1.4(5)
C(4)-C(5)-C(5A)-C(6)	176.6(3)
C(9A)-C(5A)-C(6)-C(7)	-1.5(5)
C(5)-C(5A)-C(6)-C(7)	-179.5(4)
C(5A)-C(6)-C(7)-C(8)	0.4(6)
C(6)-C(7)-C(8)-C(9)	0.8(6)

C(7)-C(8)-C(9)-C(9A)	-0.9(6)
C(8)-C(9)-C(9A)-C(5A)	-0.3(6)
C(8)-C(9)-C(9A)-C(9B)	177.6(4)
C(6)-C(5A)-C(9A)-C(9)	1.5(5)
C(5)-C(5A)-C(9A)-C(9)	179.5(3)
C(6)-C(5A)-C(9A)-C(9B)	-176.5(3)
C(5)-C(5A)-C(9A)-C(9B)	1.5(5)
C(3)-C(3A)-C(9B)-N	-1.3(5)
C(4)-C(3A)-C(9B)-N	179.4(3)
C(3)-C(3A)-C(9B)-C(9A)	178.8(3)
C(4)-C(3A)-C(9B)-C(9A)	-0.5(5)
C(9)-C(9A)-C(9B)-N	1.6(5)
C(5A)-C(9A)-C(9B)-N	179.5(3)
C(9)-C(9A)-C(9B)-C(3A)	-178.5(3)
C(5A)-C(9A)-C(9B)-C(3A)	-0.6(5)
C(5)-C(4)-C(10)-O(1)	91.4(4)
C(3A)-C(4)-C(10)-O(1)	-90.4(4)
C(5)-C(4)-C(10)-Cr	-86.6(4)
C(3A)-C(4)-C(10)-Cr	91.6(4)
O(3)-C(13)-Cr-C(16)	-134(5)
O(3)-C(13)-Cr-C(15)	65(7)
O(3)-C(13)-Cr-C(14)	47(5)
O(3)-C(13)-Cr-C(12)	-46(5)
O(3)-C(13)-Cr-C(10)	138(5)
O(6)-C(16)-Cr-C(13)	147(17)
O(6)-C(16)-Cr-C(15)	-34(17)
O(6)-C(16)-Cr-C(14)	174(100)
O(6)-C(16)-Cr-C(12)	55(17)
O(6)-C(16)-Cr-C(10)	-124(17)
O(5)-C(15)-Cr-C(13)	-129(11)

O(5)-C(15)-Cr-C(16)	70(12)
O(5)-C(15)-Cr-C(14)	-111(12)
O(5)-C(15)-Cr-C(12)	-18(12)
O(5)-C(15)-Cr-C(10)	159(12)
O(4)-C(14)-Cr-C(13)	29(5)
O(4)-C(14)-Cr-C(16)	2(8)
O(4)-C(14)-Cr-C(15)	-150(5)
O(4)-C(14)-Cr-C(12)	121(5)
O(4)-C(14)-Cr-C(10)	-60(5)
O(2)-C(12)-Cr-C(13)	-68(9)
O(2)-C(12)-Cr-C(16)	25(9)
O(2)-C(12)-Cr-C(15)	115(9)
O(2)-C(12)-Cr-C(14)	-153(9)
O(2)-C(12)-Cr-C(10)	37(10)
O(1)-C(10)-Cr-C(13)	-5.3(3)
C(4)-C(10)-Cr-C(13)	172.6(3)
O(1)-C(10)-Cr-C(16)	-98.0(3)
C(4)-C(10)-Cr-C(16)	79.9(3)
O(1)-C(10)-Cr-C(15)	172.2(3)
C(4)-C(10)-Cr-C(15)	-9.9(3)
O(1)-C(10)-Cr-C(14)	79.6(3)
C(4)-C(10)-Cr-C(14)	-102.5(3)
O(1)-C(10)-Cr-C(12)	-110(3)
C(4)-C(10)-Cr-C(12)	68(3)
C(2)-C(1)-N-C(9B)	-1.1(6)
C(3A)-C(9B)-N-C(1)	1.2(5)
C(9A)-C(9B)-N-C(1)	-178.9(3)
C(4)-C(10)-O(1)-C(11)	0.4(4)
Cr-C(10)-O(1)-C(11)	178.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **29** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.13 tricarbonyl(ŋ^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline)chromium(0) (30)

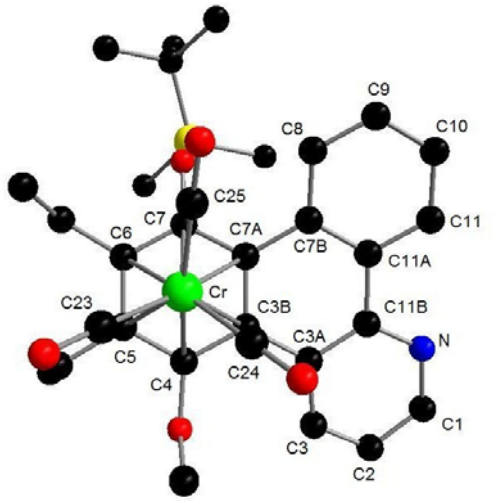


Table 1. Crystal data and structure refinement for **30**.

Formula weight	413.30
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 6.6296(4) A alpha = 90 deg.
	b = 11.1970(9) A beta = 90.670(4) deg.
	c = 23.8845(18) A gamma = 90 deg.
Volume	1772.9(2) A^3
Z, Calculated density	4, 1.548 Mg/m^3
Absorption coefficient	0.684 mm^-1
F(000)	840
Crystal size	0.48 x 0.08 x 0.04 mm
Theta range for data collection	2.01 to 27.50 deg.

Limiting indices	-8<=h<=7, -13<=k<=14, -31<=l<=21
Reflections collected / unique	9732 / 4039 [R(int) = 0.0781]
Completeness to theta = 27.50	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.95170 and 0.81388
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4039 / 0 / 253
Goodness-of-fit on F^2	0.942
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1103
R indices (all data)	R1 = 0.1181, wR2 = 0.1297
Largest diff. peak and hole	0.360 and -0.608 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **30**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8697(5)	893(3)	2447(2)	30(1)
C(2)	9378(5)	1060(3)	1902(2)	30(1)
C(3)	8306(5)	1787(3)	1547(2)	27(1)
C(3A)	6517(5)	2328(3)	1743(2)	22(1)
C(4)	5287(5)	3102(3)	1392(2)	22(1)
C(5)	3602(5)	3620(3)	1607(2)	24(1)
C(5A)	3006(5)	3428(3)	2172(2)	23(1)
C(6)	1306(5)	4025(3)	2398(2)	28(1)
C(7)	761(5)	3843(3)	2936(2)	30(1)
C(8)	1884(6)	3063(4)	3280(2)	36(1)
C(9)	3543(5)	2496(3)	3075(2)	30(1)
C(9A)	4142(5)	2665(3)	2522(2)	24(1)

C(9B)	5947(5)	2115(3)	2294(2)	23(1)
C(10)	5800(5)	3315(3)	791(2)	24(1)
C(11)	7788(5)	4994(4)	1156(2)	32(1)
C(12)	3607(5)	1509(3)	-474(2)	27(1)
C(13)	5976(5)	3477(3)	-347(2)	25(1)
C(14)	7265(5)	1547(3)	100(2)	26(1)
C(15)	3663(5)	1227(3)	638(2)	26(1)
C(16)	2332(5)	3262(4)	170(2)	28(1)
Cr	4764(1)	2371(1)	139(1)	23(1)
N	7030(4)	1388(3)	2644(1)	28(1)
O(1)	7006(3)	4240(2)	699(1)	28(1)
O(2)	2876(4)	1025(3)	-845(1)	38(1)
O(3)	6749(4)	4107(2)	-660(1)	33(1)
O(4)	8825(4)	1106(2)	72(1)	38(1)
O(5)	2968(4)	527(3)	929(1)	37(1)
O(6)	843(4)	3783(2)	190(1)	40(1)

Table 3. Bond lengths [A] and angles [deg] for **30**.

C(1)-N	1.327(4)
C(1)-C(2)	1.395(5)
C(1)-H(1)	0.9500
C(2)-C(3)	1.369(5)
C(2)-H(2)	0.9500
C(3)-C(3A)	1.416(5)
C(3)-H(3)	0.9500
C(3A)-C(9B)	1.393(5)
C(3A)-C(4)	1.450(5)
C(4)-C(5)	1.364(5)

C(4)-C(10)	1.499(5)
C(5)-C(5A)	1.427(5)
C(5)-H(5)	0.9500
C(5A)-C(9A)	1.408(5)
C(5A)-C(6)	1.422(5)
C(6)-C(7)	1.354(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.407(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.365(5)
C(8)-H(8)	0.9500
C(9)-C(9A)	1.396(5)
C(9)-H(9)	0.9500
C(9A)-C(9B)	1.458(5)
C(9B)-N	1.365(4)
C(10)-O(1)	1.328(4)
C(10)-Cr	1.998(4)
C(11)-O(1)	1.469(4)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-O(2)	1.141(4)
C(12)-Cr	1.907(4)
C(13)-O(3)	1.153(4)
C(13)-Cr	1.884(4)
C(14)-O(4)	1.149(4)
C(14)-Cr	1.900(4)
C(15)-O(5)	1.148(4)
C(15)-Cr	1.900(4)
C(16)-O(6)	1.148(4)

C(16)-Cr	1.898(4)
N-C(1)-C(2)	123.6(4)
N-C(1)-H(1)	118.2
C(2)-C(1)-H(1)	118.2
C(3)-C(2)-C(1)	119.1(4)
C(3)-C(2)-H(2)	120.5
C(1)-C(2)-H(2)	120.5
C(2)-C(3)-C(3A)	118.7(4)
C(2)-C(3)-H(3)	120.6
C(3A)-C(3)-H(3)	120.6
C(9B)-C(3A)-C(3)	118.4(3)
C(9B)-C(3A)-C(4)	119.4(3)
C(3)-C(3A)-C(4)	122.1(3)
C(5)-C(4)-C(3A)	119.6(3)
C(5)-C(4)-C(10)	119.2(3)
C(3A)-C(4)-C(10)	121.1(3)
C(4)-C(5)-C(5A)	121.9(3)
C(4)-C(5)-H(5)	119.1
C(5A)-C(5)-H(5)	119.1
C(9A)-C(5A)-C(6)	118.8(3)
C(9A)-C(5A)-C(5)	120.1(3)
C(6)-C(5A)-C(5)	121.1(3)
C(7)-C(6)-C(5A)	120.7(4)
C(7)-C(6)-H(6)	119.7
C(5A)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	120.1(4)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	120.2(4)
C(9)-C(8)-H(8)	119.9

C(7)-C(8)-H(8) 119.9

C(8)-C(9)-C(9A) 121.0(4)

C(8)-C(9)-H(9) 119.5

C(9A)-C(9)-H(9) 119.5

C(9)-C(9A)-C(5A) 119.2(3)

C(9)-C(9A)-C(9B) 122.7(3)

C(5A)-C(9A)-C(9B) 118.0(3)

N-C(9B)-C(3A) 122.3(3)

N-C(9B)-C(9A) 116.8(3)

C(3A)-C(9B)-C(9A) 120.9(3)

O(1)-C(10)-C(4) 115.2(3)

O(1)-C(10)-Cr 119.1(3)

C(4)-C(10)-Cr 125.6(3)

O(1)-C(11)-H(11A) 109.5

O(1)-C(11)-H(11B) 109.5

H(11A)-C(11)-H(11B) 109.5

O(1)-C(11)-H(11C) 109.5

H(11A)-C(11)-H(11C) 109.5

H(11B)-C(11)-H(11C) 109.5

O(2)-C(12)-Cr 177.8(3)

O(3)-C(13)-Cr 176.6(3)

O(4)-C(14)-Cr 176.4(3)

O(5)-C(15)-Cr 178.4(3)

O(6)-C(16)-Cr 178.8(3)

C(13)-Cr-C(16) 92.72(15)

C(13)-Cr-C(15) 177.31(15)

C(16)-Cr-C(15) 89.83(15)

C(13)-Cr-C(14) 84.85(16)

C(16)-Cr-C(14) 177.27(16)

C(15)-Cr-C(14) 92.58(15)

C(13)-Cr-C(12)	91.71(16)
C(16)-Cr-C(12)	87.84(16)
C(15)-Cr-C(12)	89.26(16)
C(14)-Cr-C(12)	93.45(15)
C(13)-Cr-C(10)	89.24(16)
C(16)-Cr-C(10)	88.58(15)
C(15)-Cr-C(10)	89.95(16)
C(14)-Cr-C(10)	90.15(15)
C(12)-Cr-C(10)	176.34(14)
C(1)-N-C(9B)	117.8(3)
C(10)-O(1)-C(11)	122.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **30**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	27(2)	31(2)	32(3)	3(2)	-5(2)	5(2)
C(2)	25(2)	31(2)	35(3)	5(2)	1(2)	10(2)
C(3)	21(2)	31(2)	29(2)	2(2)	1(2)	1(2)
C(3A)	20(2)	24(2)	22(2)	-1(2)	-3(1)	0(2)
C(4)	21(2)	25(2)	22(2)	0(2)	-3(2)	-3(2)
C(5)	18(2)	31(2)	24(2)	2(2)	-4(2)	0(2)
C(5A)	19(2)	25(2)	24(2)	0(2)	-2(1)	-1(2)
C(6)	20(2)	33(2)	31(2)	1(2)	-3(2)	2(2)
C(7)	26(2)	35(2)	29(2)	-3(2)	4(2)	5(2)
C(8)	38(2)	41(3)	28(2)	6(2)	9(2)	7(2)

C(9)	28(2)	31(2)	31(2)	6(2)	0(2)	6(2)
C(9A)	22(2)	24(2)	25(2)	1(2)	-1(1)	0(2)
C(9B)	20(2)	22(2)	25(2)	1(2)	-2(2)	0(2)
C(10)	12(2)	28(2)	33(2)	3(2)	-5(2)	6(2)
C(11)	26(2)	41(2)	28(3)	-8(2)	-6(2)	-14(2)
C(12)	27(2)	25(2)	28(2)	0(2)	5(2)	0(2)
C(13)	25(2)	31(2)	21(2)	-5(2)	-2(2)	6(2)
C(14)	28(2)	25(2)	26(2)	-3(2)	1(2)	-4(2)
C(15)	23(2)	30(2)	27(2)	0(2)	-1(2)	5(2)
C(16)	25(2)	32(2)	27(2)	0(2)	-1(2)	-5(2)
Cr	18(1)	26(1)	24(1)	0(1)	-1(1)	1(1)
N	24(2)	31(2)	30(2)	5(2)	-3(1)	4(1)
O(1)	22(1)	35(2)	28(2)	-3(1)	-2(1)	-10(1)
O(2)	38(2)	45(2)	32(2)	-12(2)	-2(1)	-12(1)
O(3)	36(2)	33(2)	28(2)	6(1)	-1(1)	-5(1)
O(4)	25(1)	36(2)	53(2)	-5(2)	5(1)	6(1)
O(5)	38(2)	37(2)	37(2)	8(2)	6(1)	-5(1)
O(6)	21(1)	42(2)	57(2)	-5(2)	-3(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **30**.

	x	y	z	U(eq)
H(1)	9470	397	2691	36
H(2)	10569	674	1779	36
H(3)	8753	1927	1177	33
H(5)	2802	4124	1374	29
H(6)	545	4557	2169	33

H(7)	-383	4244	3081	36
H(8)	1487	2929	3655	43
H(9)	4302	1980	3313	36
H(11A)	8586	4504	1417	48
H(11B)	6659	5357	1355	48
H(11C)	8643	5624	1001	48

Table 6. Torsion angles [deg] for **30**.

N-C(1)-C(2)-C(3)	1.2(6)
C(1)-C(2)-C(3)-C(3A)	-1.2(6)
C(2)-C(3)-C(3A)-C(9B)	1.3(5)
C(2)-C(3)-C(3A)-C(4)	-179.5(3)
C(9B)-C(3A)-C(4)-C(5)	0.7(5)
C(3)-C(3A)-C(4)-C(5)	-178.5(3)
C(9B)-C(3A)-C(4)-C(10)	-177.5(3)
C(3)-C(3A)-C(4)-C(10)	3.3(5)
C(3A)-C(4)-C(5)-C(5A)	0.2(5)
C(10)-C(4)-C(5)-C(5A)	178.4(3)
C(4)-C(5)-C(5A)-C(9A)	-1.4(5)
C(4)-C(5)-C(5A)-C(6)	176.6(3)
C(9A)-C(5A)-C(6)-C(7)	-1.5(5)
C(5)-C(5A)-C(6)-C(7)	-179.5(4)
C(5A)-C(6)-C(7)-C(8)	0.4(6)
C(6)-C(7)-C(8)-C(9)	0.8(6)
C(7)-C(8)-C(9)-C(9A)	-0.9(6)
C(8)-C(9)-C(9A)-C(5A)	-0.3(6)
C(8)-C(9)-C(9A)-C(9B)	177.6(4)
C(6)-C(5A)-C(9A)-C(9)	1.5(5)

C(5)-C(5A)-C(9A)-C(9)	179.5(3)
C(6)-C(5A)-C(9A)-C(9B)	-176.5(3)
C(5)-C(5A)-C(9A)-C(9B)	1.5(5)
C(3)-C(3A)-C(9B)-N	-1.3(5)
C(4)-C(3A)-C(9B)-N	179.4(3)
C(3)-C(3A)-C(9B)-C(9A)	178.8(3)
C(4)-C(3A)-C(9B)-C(9A)	-0.5(5)
C(9)-C(9A)-C(9B)-N	1.6(5)
C(5A)-C(9A)-C(9B)-N	179.5(3)
C(9)-C(9A)-C(9B)-C(3A)	-178.5(3)
C(5A)-C(9A)-C(9B)-C(3A)	-0.6(5)
C(5)-C(4)-C(10)-O(1)	91.4(4)
C(3A)-C(4)-C(10)-O(1)	-90.4(4)
C(5)-C(4)-C(10)-Cr	-86.6(4)
C(3A)-C(4)-C(10)-Cr	91.6(4)
O(3)-C(13)-Cr-C(16)	-134(5)
O(3)-C(13)-Cr-C(15)	65(7)
O(3)-C(13)-Cr-C(14)	47(5)
O(3)-C(13)-Cr-C(12)	-46(5)
O(3)-C(13)-Cr-C(10)	138(5)
O(6)-C(16)-Cr-C(13)	147(17)
O(6)-C(16)-Cr-C(15)	-34(17)
O(6)-C(16)-Cr-C(14)	174(100)
O(6)-C(16)-Cr-C(12)	55(17)
O(6)-C(16)-Cr-C(10)	-124(17)
O(5)-C(15)-Cr-C(13)	-129(11)
O(5)-C(15)-Cr-C(16)	70(12)
O(5)-C(15)-Cr-C(14)	-111(12)
O(5)-C(15)-Cr-C(12)	-18(12)
O(5)-C(15)-Cr-C(10)	159(12)

O(4)-C(14)-Cr-C(13)	29(5)
O(4)-C(14)-Cr-C(16)	2(8)
O(4)-C(14)-Cr-C(15)	-150(5)
O(4)-C(14)-Cr-C(12)	121(5)
O(4)-C(14)-Cr-C(10)	-60(5)
O(2)-C(12)-Cr-C(13)	-68(9)
O(2)-C(12)-Cr-C(16)	25(9)
O(2)-C(12)-Cr-C(15)	115(9)
O(2)-C(12)-Cr-C(14)	-153(9)
O(2)-C(12)-Cr-C(10)	37(10)
O(1)-C(10)-Cr-C(13)	-5.3(3)
C(4)-C(10)-Cr-C(13)	172.6(3)
O(1)-C(10)-Cr-C(16)	-98.0(3)
C(4)-C(10)-Cr-C(16)	79.9(3)
O(1)-C(10)-Cr-C(15)	172.2(3)
C(4)-C(10)-Cr-C(15)	-9.9(3)
O(1)-C(10)-Cr-C(14)	79.6(3)
C(4)-C(10)-Cr-C(14)	-102.5(3)
O(1)-C(10)-Cr-C(12)	-110(3)
C(4)-C(10)-Cr-C(12)	68(3)
C(2)-C(1)-N-C(9B)	-1.1(6)
C(3A)-C(9B)-N-C(1)	1.2(5)
C(9A)-C(9B)-N-C(1)	-178.9(3)
C(4)-C(10)-O(1)-C(11)	0.4(4)
Cr-C(10)-O(1)-C(11)	178.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **30** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.14 tricarbonyl(ŋ^6-7b,8,9,10,11,11a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline)chromium(0) (31)

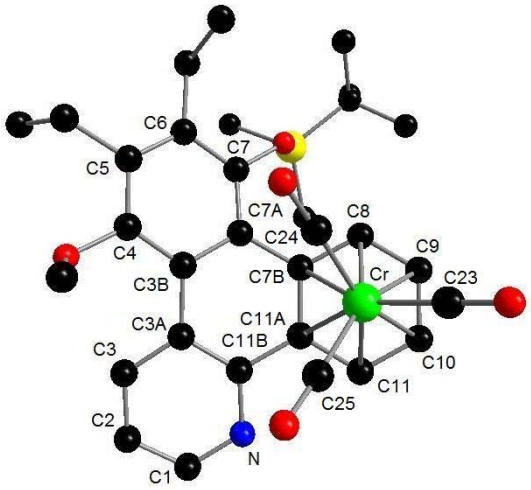


Table 1. Crystal data and structure refinement for **31**.

Device Type	STOE IPDS 2T
Empirical formula	C32 H35 Cl2 Cr N O5 Si
Formula weight	664.60
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 8.9672(2) A alpha = 90 deg.
	b = 37.3182(5) A beta = 110.588(2) deg.
	c = 10.4100(2) A gamma = 90 deg.
Volume	3261.11(11) A^3
Z, Calculated density	4, 1.354 Mg/m^3
Absorption coefficient	0.591 mm^-1
F(000)	1384
Crystal size	0.40 x 0.10 x 0.10 mm
Theta range for data collection	2.16 to 28.00 deg.
Limiting indices	-11<=h<=11, -49<=k<=49, -13<=l<=12
Reflections collected / unique	85943 / 7876 [R(int) = 0.0746]

Completeness to theta = 28.00 100.0 %

Absorption correction Integration

Max. and min. transmission 0.9665 and 0.7658

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 7876 / 0 / 387

Goodness-of-fit on F^2 1.180

Final R indices [I>2sigma(I)] R1 = 0.0645, wR2 = 0.1505

R indices (all data) R1 = 0.0755, wR2 = 0.1549

Largest diff. peak and hole 0.790 and -0.601 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **31**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3695(4)	196(1)	1316(4)	31(1)
C(2)	5166(4)	28(1)	1755(4)	32(1)
C(3)	6514(4)	237(1)	2304(4)	29(1)
C(3A)	6382(4)	609(1)	2410(3)	24(1)
C(3B)	7736(4)	850(1)	3041(3)	22(1)
C(4)	9331(4)	756(1)	3267(3)	24(1)
C(5)	10614(4)	969(1)	4033(3)	25(1)
C(6)	10327(4)	1278(1)	4671(3)	24(1)
C(7)	8746(4)	1381(1)	4418(3)	22(1)
C(7A)	7450(3)	1192(1)	3491(3)	22(1)
C(7B)	5857(3)	1352(1)	2850(3)	22(1)
C(8)	5605(4)	1731(1)	2799(3)	25(1)
C(9)	4114(4)	1879(1)	2074(3)	29(1)
C(10)	2827(4)	1655(1)	1333(4)	31(1)

C(11)	3053(4)	1288(1)	1319(3)	27(1)
C(11A)	4571(4)	1131(1)	2064(3)	24(1)
C(11B)	4823(4)	747(1)	1959(3)	24(1)
C(12)	9435(4)	490(1)	1255(4)	35(1)
C(13)	12276(4)	851(1)	4165(4)	31(1)
C(14)	12939(5)	569(1)	5288(4)	43(1)
C(15)	11663(4)	1520(1)	5525(4)	29(1)
C(16)	11922(5)	1828(1)	4662(4)	41(1)
C(17)	9680(4)	1449(1)	7900(4)	34(1)
C(18)	6159(4)	1483(1)	6252(4)	38(1)
C(19)	8141(5)	2187(1)	6913(4)	32(1)
C(20)	9633(5)	2364(1)	6816(5)	44(1)
C(21)	8133(8)	2238(1)	8369(5)	63(2)
C(22)	6652(5)	2369(1)	5899(5)	41(1)
C(23)	6958(4)	1594(1)	731(4)	32(1)
C(24)	4608(5)	1199(1)	-661(4)	39(1)
C(25)	4245(4)	1891(1)	-716(4)	35(1)
C(26)	-598(5)	413(1)	6606(5)	51(1)
Cl(1)	865(1)	487(1)	8233(1)	51(1)
Cl(2)	-2519(2)	459(1)	6616(2)	89(1)
Cr	4878(1)	1549(1)	657(1)	25(1)
N	3508(3)	546(1)	1409(3)	28(1)
O(1)	9673(3)	446(1)	2690(2)	29(1)
O(2)	8483(3)	1688(1)	5046(2)	24(1)
O(3)	8271(3)	1609(1)	810(3)	50(1)
O(4)	4490(5)	976(1)	-1454(3)	62(1)
O(5)	3855(4)	2104(1)	-1566(3)	51(1)
Si	8122(1)	1696(1)	6521(1)	24(1)

Table 3. Bond lengths [A] and angles [deg] for **31**.

C(1)-N	1.326(5)
C(1)-C(2)	1.384(5)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.381(5)
C(2)-H(2A)	0.9500
C(3)-C(3A)	1.402(4)
C(3)-H(3A)	0.9500
C(3A)-C(11B)	1.407(4)
C(3A)-C(3B)	1.468(4)
C(3B)-C(4)	1.410(4)
C(3B)-C(7A)	1.416(4)
C(4)-O(1)	1.387(4)
C(4)-C(5)	1.396(4)
C(5)-C(6)	1.397(5)
C(5)-C(13)	1.514(4)
C(6)-C(7)	1.402(4)
C(6)-C(15)	1.516(4)
C(7)-O(2)	1.380(4)
C(7)-C(7A)	1.410(4)
C(7A)-C(7B)	1.472(4)
C(7B)-C(11A)	1.420(4)
C(7B)-C(8)	1.431(4)
C(7B)-Cr	2.262(3)
C(8)-C(9)	1.398(4)
C(8)-Cr	2.199(3)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.413(5)
C(9)-Cr	2.209(3)
C(9)-H(9A)	0.9500

C(10)-C(11)	1.388(5)
C(10)-Cr	2.224(3)
C(10)-H(10A)	0.9500
C(11)-C(11A)	1.434(4)
C(11)-Cr	2.213(3)
C(11)-H(11A)	0.9500
C(11A)-C(11B)	1.458(4)
C(11A)-Cr	2.222(3)
C(11B)-N	1.345(4)
C(12)-O(1)	1.442(4)
C(12)-H(12C)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12A)	0.9800
C(13)-C(14)	1.528(5)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14C)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14A)	0.9800
C(15)-C(16)	1.524(5)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-Si	1.857(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-Si	1.860(4)
C(18)-H(18C)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18A)	0.9800
C(19)-C(20)	1.527(6)
C(19)-C(21)	1.529(5)
C(19)-C(22)	1.538(5)
C(19)-Si	1.877(4)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(3)	1.152(4)
C(23)-Cr	1.847(4)
C(24)-O(4)	1.152(5)
C(24)-Cr	1.846(4)
C(25)-O(5)	1.148(5)
C(25)-Cr	1.852(4)
C(26)-Cl(2)	1.734(5)
C(26)-Cl(1)	1.761(5)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
O(2)-Si	1.678(2)
N-C(1)-C(2)	123.5(3)
N-C(1)-H(1A)	118.3
C(2)-C(1)-H(1A)	118.3
C(3)-C(2)-C(1)	118.5(3)
C(3)-C(2)-H(2A)	120.8

C(1)-C(2)-H(2A) 120.8

C(2)-C(3)-C(3A) 120.3(3)

C(2)-C(3)-H(3A) 119.8

C(3A)-C(3)-H(3A) 119.8

C(3)-C(3A)-C(11B) 116.0(3)

C(3)-C(3A)-C(3B) 124.3(3)

C(11B)-C(3A)-C(3B) 119.5(3)

C(4)-C(3B)-C(7A) 117.4(3)

C(4)-C(3B)-C(3A) 123.6(3)

C(7A)-C(3B)-C(3A) 118.9(3)

O(1)-C(4)-C(5) 117.4(3)

O(1)-C(4)-C(3B) 120.1(3)

C(5)-C(4)-C(3B) 122.5(3)

C(4)-C(5)-C(6) 119.3(3)

C(4)-C(5)-C(13) 118.2(3)

C(6)-C(5)-C(13) 122.5(3)

C(5)-C(6)-C(7) 118.7(3)

C(5)-C(6)-C(15) 122.1(3)

C(7)-C(6)-C(15) 119.0(3)

O(2)-C(7)-C(6) 118.0(3)

O(2)-C(7)-C(7A) 120.1(3)

C(6)-C(7)-C(7A) 121.8(3)

C(7)-C(7A)-C(3B) 118.3(3)

C(7)-C(7A)-C(7B) 123.0(3)

C(3B)-C(7A)-C(7B) 118.3(3)

C(11A)-C(7B)-C(8) 117.8(3)

C(11A)-C(7B)-C(7A) 119.2(3)

C(8)-C(7B)-C(7A) 122.1(3)

C(11A)-C(7B)-Cr 70.04(17)

C(8)-C(7B)-Cr 68.93(17)

C(7A)-C(7B)-Cr 124.0(2)

C(9)-C(8)-C(7B) 121.4(3)

C(9)-C(8)-Cr 71.89(18)

C(7B)-C(8)-Cr 73.69(17)

C(9)-C(8)-H(8A) 119.3

C(7B)-C(8)-H(8A) 119.3

Cr-C(8)-H(8A) 127.2

C(8)-C(9)-C(10) 120.2(3)

C(8)-C(9)-Cr 71.13(18)

C(10)-C(9)-Cr 72.0(2)

C(8)-C(9)-H(9A) 119.9

C(10)-C(9)-H(9A) 119.9

Cr-C(9)-H(9A) 129.4

C(11)-C(10)-C(9) 119.7(3)

C(11)-C(10)-Cr 71.35(19)

C(9)-C(10)-Cr 70.84(19)

C(11)-C(10)-H(10A) 120.1

C(9)-C(10)-H(10A) 120.1

Cr-C(10)-H(10A) 130.2

C(10)-C(11)-C(11A) 120.8(3)

C(10)-C(11)-Cr 72.2(2)

C(11A)-C(11)-Cr 71.49(18)

C(10)-C(11)-H(11A) 119.6

C(11A)-C(11)-H(11A) 119.6

Cr-C(11)-H(11A) 129.2

C(7B)-C(11A)-C(11) 119.9(3)

C(7B)-C(11A)-C(11B) 119.8(3)

C(11)-C(11A)-C(11B) 120.2(3)

C(7B)-C(11A)-Cr 73.04(18)

C(11)-C(11A)-Cr 70.79(18)

C(11B)-C(11A)-Cr 125.5(2)

N-C(11B)-C(3A) 123.8(3)

N-C(11B)-C(11A) 116.4(3)

C(3A)-C(11B)-C(11A) 119.8(3)

O(1)-C(12)-H(12C) 109.5

O(1)-C(12)-H(12B) 109.5

H(12C)-C(12)-H(12B) 109.5

O(1)-C(12)-H(12A) 109.5

H(12C)-C(12)-H(12A) 109.5

H(12B)-C(12)-H(12A) 109.5

C(5)-C(13)-C(14) 112.1(3)

C(5)-C(13)-H(13A) 109.2

C(14)-C(13)-H(13A) 109.2

C(5)-C(13)-H(13B) 109.2

C(14)-C(13)-H(13B) 109.2

H(13A)-C(13)-H(13B) 107.9

C(13)-C(14)-H(14C) 109.5

C(13)-C(14)-H(14B) 109.5

H(14C)-C(14)-H(14B) 109.5

C(13)-C(14)-H(14A) 109.5

H(14C)-C(14)-H(14A) 109.5

H(14B)-C(14)-H(14A) 109.5

C(6)-C(15)-C(16) 110.9(3)

C(15)-C(16)-H(16A) 109.5

C(15)-C(16)-H(16B) 109.5

H(16A)-C(16)-H(16B) 109.5

C(15)-C(16)-H(16C) 109.5

H(16A)-C(16)-H(16C) 109.5

H(16B)-C(16)-H(16C) 109.5

Si-C(17)-H(17A) 109.5

Si-C(17)-H(17B) 109.5

H(17A)-C(17)-H(17B) 109.5

Si-C(17)-H(17C) 109.5

H(17A)-C(17)-H(17C) 109.5

H(17B)-C(17)-H(17C) 109.5

Si-C(18)-H(18C) 109.5

Si-C(18)-H(18B) 109.5

H(18C)-C(18)-H(18B) 109.5

Si-C(18)-H(18A) 109.5

H(18C)-C(18)-H(18A) 109.5

H(18B)-C(18)-H(18A) 109.5

C(20)-C(19)-C(21) 108.8(4)

C(20)-C(19)-C(22) 109.5(3)

C(21)-C(19)-C(22) 108.7(3)

C(20)-C(19)-Si 110.4(2)

C(21)-C(19)-Si 109.4(3)

C(22)-C(19)-Si 110.0(3)

C(19)-C(20)-H(20A) 109.5

C(19)-C(20)-H(20B) 109.5

H(20A)-C(20)-H(20B) 109.5

C(19)-C(20)-H(20C) 109.5

H(20A)-C(20)-H(20C) 109.5

H(20B)-C(20)-H(20C) 109.5

C(19)-C(21)-H(21A) 109.5

C(19)-C(21)-H(21B) 109.5

H(21A)-C(21)-H(21B) 109.5

C(19)-C(21)-H(21C) 109.5

H(21A)-C(21)-H(21C) 109.5

H(21B)-C(21)-H(21C) 109.5

C(19)-C(22)-H(22A) 109.5

C(19)-C(22)-H(22B) 109.5

H(22A)-C(22)-H(22B) 109.5

C(19)-C(22)-H(22C) 109.5

H(22A)-C(22)-H(22C) 109.5

H(22B)-C(22)-H(22C) 109.5

O(3)-C(23)-Cr 177.1(3)

O(4)-C(24)-Cr 177.5(4)

O(5)-C(25)-Cr 179.8(4)

Cl(2)-C(26)-Cl(1) 112.6(3)

Cl(2)-C(26)-H(26A) 109.1

Cl(1)-C(26)-H(26A) 109.1

Cl(2)-C(26)-H(26B) 109.1

Cl(1)-C(26)-H(26B) 109.1

H(26A)-C(26)-H(26B) 107.8

C(24)-Cr-C(23) 87.81(18)

C(24)-Cr-C(25) 89.38(17)

C(23)-Cr-C(25) 90.04(16)

C(24)-Cr-C(8) 152.43(15)

C(23)-Cr-C(8) 89.71(14)

C(25)-Cr-C(8) 118.09(15)

C(24)-Cr-C(9) 154.22(16)

C(23)-Cr-C(9) 117.86(15)

C(25)-Cr-C(9) 92.71(15)

C(8)-Cr-C(9) 36.98(12)

C(24)-Cr-C(11) 90.14(15)

C(23)-Cr-C(11) 150.88(14)

C(25)-Cr-C(11) 118.99(14)

C(8)-Cr-C(11) 78.93(12)

C(9)-Cr-C(11) 66.46(13)

C(24)-Cr-C(11A) 88.83(14)

C(23)-Cr-C(11A)	113.18(13)
C(25)-Cr-C(11A)	156.61(14)
C(8)-Cr-C(11A)	67.04(12)
C(9)-Cr-C(11A)	79.19(12)
C(11)-Cr-C(11A)	37.72(11)
C(24)-Cr-C(10)	117.05(16)
C(23)-Cr-C(10)	154.93(15)
C(25)-Cr-C(10)	93.28(15)
C(8)-Cr-C(10)	66.86(12)
C(9)-Cr-C(10)	37.19(12)
C(11)-Cr-C(10)	36.47(13)
C(11A)-Cr-C(10)	67.01(12)
C(24)-Cr-C(7B)	115.06(15)
C(23)-Cr-C(7B)	87.68(13)
C(25)-Cr-C(7B)	155.33(15)
C(8)-Cr-C(7B)	37.38(11)
C(9)-Cr-C(7B)	66.96(12)
C(11)-Cr-C(7B)	67.01(11)
C(11A)-Cr-C(7B)	36.92(11)
C(10)-Cr-C(7B)	79.02(12)
C(1)-N-C(11B)	117.9(3)
C(4)-O(1)-C(12)	112.2(3)
C(7)-O(2)-Si	124.7(2)
O(2)-Si-C(17)	111.26(14)
O(2)-Si-C(18)	109.34(15)
C(17)-Si-C(18)	108.65(18)
O(2)-Si-C(19)	103.12(14)
C(17)-Si-C(19)	111.69(17)
C(18)-Si-C(19)	112.70(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **31**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	27(2)	35(2)	30(2)	-3(1)	9(1)	-10(1)
C(2)	34(2)	29(2)	34(2)	-3(1)	12(2)	-5(1)
C(3)	24(2)	30(2)	33(2)	-1(1)	10(1)	0(1)
C(3A)	21(1)	29(2)	22(1)	-1(1)	9(1)	-2(1)
C(3B)	19(1)	27(2)	19(1)	0(1)	6(1)	-1(1)
C(4)	22(1)	27(2)	25(2)	-2(1)	9(1)	0(1)
C(5)	18(1)	32(2)	25(2)	1(1)	8(1)	1(1)
C(6)	19(1)	33(2)	21(1)	-1(1)	6(1)	-2(1)
C(7)	21(1)	26(1)	21(1)	0(1)	10(1)	1(1)
C(7A)	18(1)	29(2)	20(1)	0(1)	7(1)	0(1)
C(7B)	19(1)	30(2)	17(1)	-2(1)	9(1)	0(1)
C(8)	24(2)	31(2)	19(1)	-3(1)	6(1)	-1(1)
C(9)	29(2)	30(2)	27(2)	-2(1)	9(1)	5(1)
C(10)	21(2)	40(2)	30(2)	-1(1)	7(1)	5(1)
C(11)	18(1)	36(2)	26(2)	1(1)	6(1)	-2(1)
C(11A)	18(1)	31(2)	22(1)	2(1)	7(1)	-1(1)
C(11B)	21(1)	30(2)	20(1)	0(1)	8(1)	-3(1)
C(12)	33(2)	47(2)	29(2)	-11(2)	16(2)	-6(2)
C(13)	20(1)	40(2)	34(2)	-7(1)	11(1)	0(1)
C(14)	26(2)	54(2)	41(2)	0(2)	4(2)	11(2)
C(15)	19(1)	36(2)	31(2)	-6(1)	8(1)	-4(1)
C(16)	32(2)	42(2)	48(2)	-2(2)	15(2)	-9(2)

C(17)	34(2)	38(2)	27(2)	4(1)	9(1)	6(1)
C(18)	30(2)	48(2)	41(2)	5(2)	16(2)	-2(2)
C(19)	44(2)	29(2)	27(2)	0(1)	17(2)	5(1)
C(20)	43(2)	32(2)	49(2)	-6(2)	7(2)	-4(2)
C(21)	124(5)	41(2)	38(2)	-3(2)	46(3)	12(3)
C(22)	40(2)	33(2)	53(2)	7(2)	22(2)	10(2)
C(23)	33(2)	38(2)	27(2)	6(1)	12(1)	2(1)
C(24)	52(2)	38(2)	29(2)	-2(2)	18(2)	-11(2)
C(25)	28(2)	40(2)	34(2)	2(2)	6(2)	-4(1)
C(26)	47(2)	59(3)	46(2)	5(2)	14(2)	7(2)
Cl(1)	52(1)	41(1)	51(1)	-1(1)	9(1)	10(1)
Cl(2)	40(1)	103(1)	123(1)	35(1)	30(1)	4(1)
Cr	24(1)	28(1)	22(1)	0(1)	6(1)	-2(1)
N	23(1)	33(2)	28(1)	-1(1)	8(1)	-6(1)
O(1)	26(1)	31(1)	31(1)	-7(1)	12(1)	2(1)
O(2)	22(1)	27(1)	21(1)	-4(1)	7(1)	-1(1)
O(3)	32(1)	68(2)	54(2)	16(2)	22(1)	3(1)
O(4)	101(3)	51(2)	41(2)	-18(2)	35(2)	-22(2)
O(5)	48(2)	55(2)	42(2)	20(1)	4(1)	0(1)
Si	23(1)	27(1)	22(1)	0(1)	10(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **31**.

	x	y	z	U(eq)
H(1A)	2770	52	928	37
H(2A)	5246	-224	1680	39
H(3A)	7536	127	2610	34
H(8A)	6468	1885	3267	30

H(9A)	3965	2131	2081	34
H(10A)	1813	1756	845	37
H(11A)	2190	1138	810	32
H(12C)	9723	268	897	53
H(12B)	10106	686	1145	53
H(12A)	8313	546	747	53
H(13A)	12992	1062	4376	37
H(13B)	12253	751	3277	37
H(14C)	13971	484	5283	64
H(14B)	12196	368	5118	64
H(14A)	13077	676	6183	64
H(16A)	10936	1967	4284	61
H(16B)	12218	1731	3910	61
H(16C)	12777	1983	5238	61
H(17A)	9871	1217	7548	50
H(17B)	9323	1412	8678	50
H(17C)	10669	1589	8200	50
H(18C)	5346	1593	5455	57
H(18B)	5873	1519	7069	57
H(18A)	6225	1226	6089	57
H(20A)	10580	2260	7506	65
H(20B)	9601	2622	6981	65
H(20C)	9674	2324	5899	65
H(21A)	8170	2494	8583	95
H(21B)	9064	2118	9023	95
H(21C)	7159	2133	8433	95
H(22A)	6599	2322	4958	61
H(22B)	6710	2628	6066	61
H(22C)	5698	2272	6027	61
H(26A)	-439	586	5944	61

H(26B)	-467	169	6291	61

Table 6. Torsion angles [deg] for **31**.

N-C(1)-C(2)-C(3)	-0.8(6)
C(1)-C(2)-C(3)-C(3A)	0.0(5)
C(2)-C(3)-C(3A)-C(11B)	1.3(5)
C(2)-C(3)-C(3A)-C(3B)	176.7(3)
C(3)-C(3A)-C(3B)-C(4)	18.2(5)
C(11B)-C(3A)-C(3B)-C(4)	-166.5(3)
C(3)-C(3A)-C(3B)-C(7A)	-159.8(3)
C(11B)-C(3A)-C(3B)-C(7A)	15.5(4)
C(7A)-C(3B)-C(4)-O(1)	-171.4(3)
C(3A)-C(3B)-C(4)-O(1)	10.6(5)
C(7A)-C(3B)-C(4)-C(5)	7.0(5)
C(3A)-C(3B)-C(4)-C(5)	-171.1(3)
O(1)-C(4)-C(5)-C(6)	-177.8(3)
C(3B)-C(4)-C(5)-C(6)	3.8(5)
O(1)-C(4)-C(5)-C(13)	0.8(4)
C(3B)-C(4)-C(5)-C(13)	-177.6(3)
C(4)-C(5)-C(6)-C(7)	-5.8(5)
C(13)-C(5)-C(6)-C(7)	175.7(3)
C(4)-C(5)-C(6)-C(15)	179.6(3)
C(13)-C(5)-C(6)-C(15)	1.1(5)
C(5)-C(6)-C(7)-O(2)	-179.4(3)
C(15)-C(6)-C(7)-O(2)	-4.6(4)
C(5)-C(6)-C(7)-C(7A)	-3.1(5)
C(15)-C(6)-C(7)-C(7A)	171.7(3)
O(2)-C(7)-C(7A)-C(3B)	-169.8(3)

C(6)-C(7)-C(7A)-C(3B)	13.9(5)
O(2)-C(7)-C(7A)-C(7B)	17.4(4)
C(6)-C(7)-C(7A)-C(7B)	-158.8(3)
C(4)-C(3B)-C(7A)-C(7)	-15.4(4)
C(3A)-C(3B)-C(7A)-C(7)	162.7(3)
C(4)-C(3B)-C(7A)-C(7B)	157.7(3)
C(3A)-C(3B)-C(7A)-C(7B)	-24.2(4)
C(7)-C(7A)-C(7B)-C(11A)	-172.3(3)
C(3B)-C(7A)-C(7B)-C(11A)	15.0(4)
C(7)-C(7A)-C(7B)-C(8)	18.2(5)
C(3B)-C(7A)-C(7B)-C(8)	-154.5(3)
C(7)-C(7A)-C(7B)-Cr	103.2(3)
C(3B)-C(7A)-C(7B)-Cr	-69.6(3)
C(11A)-C(7B)-C(8)-C(9)	4.2(5)
C(7A)-C(7B)-C(8)-C(9)	173.8(3)
Cr-C(7B)-C(8)-C(9)	56.1(3)
C(11A)-C(7B)-C(8)-Cr	-51.9(2)
C(7A)-C(7B)-C(8)-Cr	117.8(3)
C(7B)-C(8)-C(9)-C(10)	-2.2(5)
Cr-C(8)-C(9)-C(10)	54.8(3)
C(7B)-C(8)-C(9)-Cr	-56.9(3)
C(8)-C(9)-C(10)-C(11)	-0.4(5)
Cr-C(9)-C(10)-C(11)	54.0(3)
C(8)-C(9)-C(10)-Cr	-54.4(3)
C(9)-C(10)-C(11)-C(11A)	0.8(5)
Cr-C(10)-C(11)-C(11A)	54.5(3)
C(9)-C(10)-C(11)-Cr	-53.7(3)
C(8)-C(7B)-C(11A)-C(11)	-3.7(4)
C(7A)-C(7B)-C(11A)-C(11)	-173.7(3)
Cr-C(7B)-C(11A)-C(11)	-55.1(3)

C(8)-C(7B)-C(11A)-C(11B)	173.1(3)
C(7A)-C(7B)-C(11A)-C(11B)	3.1(4)
Cr-C(7B)-C(11A)-C(11B)	121.7(3)
C(8)-C(7B)-C(11A)-Cr	51.4(2)
C(7A)-C(7B)-C(11A)-Cr	-118.6(3)
C(10)-C(11)-C(11A)-C(7B)	1.3(5)
Cr-C(11)-C(11A)-C(7B)	56.2(3)
C(10)-C(11)-C(11A)-C(11B)	-175.5(3)
Cr-C(11)-C(11A)-C(11B)	-120.6(3)
C(10)-C(11)-C(11A)-Cr	-54.9(3)
C(3)-C(3A)-C(11B)-N	-2.2(5)
C(3B)-C(3A)-C(11B)-N	-177.8(3)
C(3)-C(3A)-C(11B)-C(11A)	178.5(3)
C(3B)-C(3A)-C(11B)-C(11A)	2.8(4)
C(7B)-C(11A)-C(11B)-N	168.6(3)
C(11)-C(11A)-C(11B)-N	-14.6(4)
Cr-C(11A)-C(11B)-N	-101.7(3)
C(7B)-C(11A)-C(11B)-C(3A)	-12.0(4)
C(11)-C(11A)-C(11B)-C(3A)	164.8(3)
Cr-C(11A)-C(11B)-C(3A)	77.7(4)
C(4)-C(5)-C(13)-C(14)	-82.1(4)
C(6)-C(5)-C(13)-C(14)	96.4(4)
C(5)-C(6)-C(15)-C(16)	94.2(4)
C(7)-C(6)-C(15)-C(16)	-80.4(4)
O(4)-C(24)-Cr-C(23)	49(9)
O(4)-C(24)-Cr-C(25)	139(9)
O(4)-C(24)-Cr-C(8)	-37(9)
O(4)-C(24)-Cr-C(9)	-126(9)
O(4)-C(24)-Cr-C(11)	-102(9)
O(4)-C(24)-Cr-C(11A)	-65(9)

O(4)-C(24)-Cr-C(10)	-128(9)
O(4)-C(24)-Cr-C(7B)	-38(9)
O(3)-C(23)-Cr-C(24)	-78(8)
O(3)-C(23)-Cr-C(25)	-168(8)
O(3)-C(23)-Cr-C(8)	74(8)
O(3)-C(23)-Cr-C(9)	99(8)
O(3)-C(23)-Cr-C(11)	8(8)
O(3)-C(23)-Cr-C(11A)	10(8)
O(3)-C(23)-Cr-C(10)	95(8)
O(3)-C(23)-Cr-C(7B)	37(8)
O(5)-C(25)-Cr-C(24)	-121(100)
O(5)-C(25)-Cr-C(23)	-33(100)
O(5)-C(25)-Cr-C(8)	57(100)
O(5)-C(25)-Cr-C(9)	85(100)
O(5)-C(25)-Cr-C(11)	149(100)
O(5)-C(25)-Cr-C(11A)	154(100)
O(5)-C(25)-Cr-C(10)	122(100)
O(5)-C(25)-Cr-C(7B)	52(100)
C(9)-C(8)-Cr-C(24)	-133.7(3)
C(7B)-C(8)-Cr-C(24)	-1.9(4)
C(9)-C(8)-Cr-C(23)	141.6(2)
C(7B)-C(8)-Cr-C(23)	-86.6(2)
C(9)-C(8)-Cr-C(25)	51.7(2)
C(7B)-C(8)-Cr-C(25)	-176.46(19)
C(7B)-C(8)-Cr-C(9)	131.8(3)
C(9)-C(8)-Cr-C(11)	-65.4(2)
C(7B)-C(8)-Cr-C(11)	66.46(18)
C(9)-C(8)-Cr-C(11A)	-102.9(2)
C(7B)-C(8)-Cr-C(11A)	28.88(17)
C(9)-C(8)-Cr-C(10)	-29.2(2)

C(7B)-C(8)-Cr-C(10)	102.6(2)
C(9)-C(8)-Cr-C(7B)	-131.8(3)
C(8)-C(9)-Cr-C(24)	129.7(4)
C(10)-C(9)-Cr-C(24)	-2.3(4)
C(8)-C(9)-Cr-C(23)	-44.6(2)
C(10)-C(9)-Cr-C(23)	-176.7(2)
C(8)-C(9)-Cr-C(25)	-136.1(2)
C(10)-C(9)-Cr-C(25)	91.8(2)
C(10)-C(9)-Cr-C(8)	-132.0(3)
C(8)-C(9)-Cr-C(11)	103.3(2)
C(10)-C(9)-Cr-C(11)	-28.7(2)
C(8)-C(9)-Cr-C(11A)	66.0(2)
C(10)-C(9)-Cr-C(11A)	-66.0(2)
C(8)-C(9)-Cr-C(10)	132.0(3)
C(8)-C(9)-Cr-C(7B)	29.44(19)
C(10)-C(9)-Cr-C(7B)	-102.6(2)
C(10)-C(11)-Cr-C(24)	-139.6(2)
C(11A)-C(11)-Cr-C(24)	87.9(2)
C(10)-C(11)-Cr-C(23)	134.6(3)
C(11A)-C(11)-Cr-C(23)	2.2(4)
C(10)-C(11)-Cr-C(25)	-50.2(3)
C(11A)-C(11)-Cr-C(25)	177.3(2)
C(10)-C(11)-Cr-C(8)	65.9(2)
C(11A)-C(11)-Cr-C(8)	-66.62(19)
C(10)-C(11)-Cr-C(9)	29.25(19)
C(11A)-C(11)-Cr-C(9)	-103.2(2)
C(10)-C(11)-Cr-C(11A)	132.5(3)
C(11A)-C(11)-Cr-C(10)	-132.5(3)
C(10)-C(11)-Cr-C(7B)	103.1(2)
C(11A)-C(11)-Cr-C(7B)	-29.42(18)

C(7B)-C(11A)-Cr-C(24)	137.1(2)
C(11)-C(11A)-Cr-C(24)	-91.7(2)
C(11B)-C(11A)-Cr-C(24)	22.2(3)
C(7B)-C(11A)-Cr-C(23)	50.0(2)
C(11)-C(11A)-Cr-C(23)	-178.9(2)
C(11B)-C(11A)-Cr-C(23)	-64.9(3)
C(7B)-C(11A)-Cr-C(25)	-137.2(4)
C(11)-C(11A)-Cr-C(25)	-6.0(5)
C(11B)-C(11A)-Cr-C(25)	107.9(4)
C(7B)-C(11A)-Cr-C(8)	-29.21(17)
C(11)-C(11A)-Cr-C(8)	102.0(2)
C(11B)-C(11A)-Cr-C(8)	-144.1(3)
C(7B)-C(11A)-Cr-C(9)	-65.85(19)
C(11)-C(11A)-Cr-C(9)	65.3(2)
C(11B)-C(11A)-Cr-C(9)	179.3(3)
C(7B)-C(11A)-Cr-C(11)	-131.2(3)
C(11B)-C(11A)-Cr-C(11)	113.9(3)
C(7B)-C(11A)-Cr-C(10)	-102.7(2)
C(11)-C(11A)-Cr-C(10)	28.44(19)
C(11B)-C(11A)-Cr-C(10)	142.4(3)
C(11)-C(11A)-Cr-C(7B)	131.2(3)
C(11B)-C(11A)-Cr-C(7B)	-114.9(3)
C(11)-C(10)-Cr-C(24)	46.7(2)
C(9)-C(10)-Cr-C(24)	178.9(2)
C(11)-C(10)-Cr-C(23)	-125.2(3)
C(9)-C(10)-Cr-C(23)	7.0(4)
C(11)-C(10)-Cr-C(25)	137.7(2)
C(9)-C(10)-Cr-C(25)	-90.2(2)
C(11)-C(10)-Cr-C(8)	-103.1(2)
C(9)-C(10)-Cr-C(8)	29.06(19)

C(11)-C(10)-Cr-C(9)	-132.2(3)
C(9)-C(10)-Cr-C(11)	132.2(3)
C(11)-C(10)-Cr-C(11A)	-29.35(19)
C(9)-C(10)-Cr-C(11A)	102.8(2)
C(11)-C(10)-Cr-C(7B)	-66.0(2)
C(9)-C(10)-Cr-C(7B)	66.2(2)
C(11A)-C(7B)-Cr-C(24)	-48.7(2)
C(8)-C(7B)-Cr-C(24)	179.0(2)
C(7A)-C(7B)-Cr-C(24)	63.7(3)
C(11A)-C(7B)-Cr-C(23)	-135.2(2)
C(8)-C(7B)-Cr-C(23)	92.5(2)
C(7A)-C(7B)-Cr-C(23)	-22.8(3)
C(11A)-C(7B)-Cr-C(25)	139.7(3)
C(8)-C(7B)-Cr-C(25)	7.5(4)
C(7A)-C(7B)-Cr-C(25)	-107.8(4)
C(11A)-C(7B)-Cr-C(8)	132.2(3)
C(7A)-C(7B)-Cr-C(8)	-115.3(3)
C(11A)-C(7B)-Cr-C(9)	103.1(2)
C(8)-C(7B)-Cr-C(9)	-29.15(18)
C(7A)-C(7B)-Cr-C(9)	-144.4(3)
C(11A)-C(7B)-Cr-C(11)	30.02(18)
C(8)-C(7B)-Cr-C(11)	-102.2(2)
C(7A)-C(7B)-Cr-C(11)	142.5(3)
C(8)-C(7B)-Cr-C(11A)	-132.2(3)
C(7A)-C(7B)-Cr-C(11A)	112.5(3)
C(11A)-C(7B)-Cr-C(10)	66.16(19)
C(8)-C(7B)-Cr-C(10)	-66.08(19)
C(7A)-C(7B)-Cr-C(10)	178.6(3)
C(2)-C(1)-N-C(11B)	0.0(5)
C(3A)-C(11B)-N-C(1)	1.5(5)

C(11A)-C(11B)-N-C(1)	-179.1(3)
C(5)-C(4)-O(1)-C(12)	-100.1(3)
C(3B)-C(4)-O(1)-C(12)	78.3(4)
C(6)-C(7)-O(2)-Si	-95.9(3)
C(7A)-C(7)-O(2)-Si	87.7(3)
C(7)-O(2)-Si-C(17)	53.1(3)
C(7)-O(2)-Si-C(18)	-66.9(3)
C(7)-O(2)-Si-C(19)	173.0(2)
C(20)-C(19)-Si-O(2)	-49.9(3)
C(21)-C(19)-Si-O(2)	-169.6(3)
C(22)-C(19)-Si-O(2)	71.1(3)
C(20)-C(19)-Si-C(17)	69.7(3)
C(21)-C(19)-Si-C(17)	-50.0(4)
C(22)-C(19)-Si-C(17)	-169.4(3)
C(20)-C(19)-Si-C(18)	-167.7(3)
C(21)-C(19)-Si-C(18)	72.6(4)
C(22)-C(19)-Si-C(18)	-46.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **31** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.15 Tetracarbonyl{4-bromobenzo[*h*]quinoline-κC^9-κ*N*}manganese(I) (32)

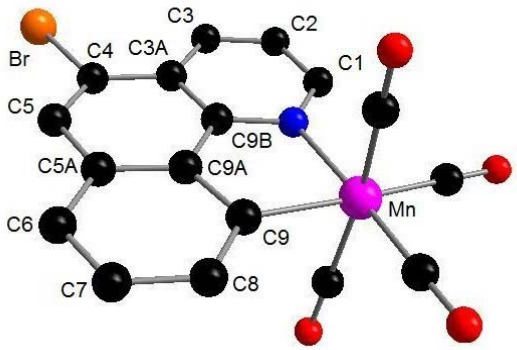


Table 1. Crystal data and structure refinement for **32**.

Empirical formula	C17 H7 Br Mn N O4
Formula weight	424.09
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 6.4995(4) A alpha = 92.791(4) deg.
	b = 10.8762(9) A beta = 104.229(5) deg.
	c = 11.2558(11) A gamma = 100.301(5) deg.
Volume	755.24(11) A^3
Z, Calculated density	2, 1.865 Mg/m^3
Absorption coefficient	3.540 mm^-1
F(000)	416
Crystal size	0.48 x 0.16 x 0.08 mm
Theta range for data collection	2.81 to 28.99 deg.
Limiting indices	-8<=h<=8, -14<=k<=14, -13<=l<=15
Reflections collected / unique	8727 / 3881 [R(int) = 0.0434]
Completeness to theta = 28.99	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.57818 and 0.48422
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3881 / 0 / 217

Goodness-of-fit on F^2 1.026

Final R indices [I>2sigma(I)] R1 = 0.0370, wR2 = 0.0945

R indices (all data) R1 = 0.0548, wR2 = 0.1005

Largest diff. peak and hole 1.646 and -0.465 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **32**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-2739(4)	2290(3)	1315(3)	27(1)
C(2)	-3653(4)	3267(3)	787(3)	30(1)
C(3)	-2448(4)	4451(3)	954(3)	28(1)
C(3A)	-253(4)	4669(3)	1636(3)	23(1)
C(4)	1220(4)	5852(3)	1888(3)	24(1)
C(5)	3301(4)	5990(3)	2545(3)	24(1)
C(5A)	4157(4)	4934(3)	3030(3)	23(1)
C(6)	6301(4)	5019(3)	3708(3)	27(1)
C(7)	6975(4)	3951(3)	4149(3)	28(1)
C(8)	5555(4)	2776(3)	3928(3)	24(1)
C(9)	3412(4)	2632(3)	3248(3)	22(1)
C(9A)	2750(4)	3746(3)	2813(3)	20(1)
C(9B)	550(4)	3634(2)	2130(3)	20(1)
C(10)	-1581(5)	-122(3)	2387(3)	27(1)
C(11)	2578(4)	17(3)	3451(3)	24(1)
C(12)	617(4)	1567(3)	4340(3)	26(1)
C(13)	1752(4)	820(2)	1368(3)	22(1)
Br	177(1)	7285(1)	1272(1)	33(1)
Mn	900(1)	1097(1)	2785(1)	21(1)

N	-690(3)	2457(2)	1976(2)	22(1)
O(1)	-3134(3)	-888(2)	2144(2)	33(1)
O(2)	3680(3)	-664(2)	3839(2)	33(1)
O(3)	580(3)	1860(2)	5316(2)	34(1)
O(4)	2388(3)	643(2)	527(2)	31(1)

Table 3. Bond lengths [A] and angles [deg] for **32**.

C(1)-N	1.331(3)
C(1)-C(2)	1.395(4)
C(1)-H(1)	0.9500
C(2)-C(3)	1.360(4)
C(2)-H(2)	0.9500
C(3)-C(3A)	1.415(4)
C(3)-H(3)	0.9500
C(3A)-C(9B)	1.406(4)
C(3A)-C(4)	1.430(4)
C(4)-C(5)	1.351(4)
C(4)-Br	1.903(3)
C(5)-C(5A)	1.438(4)
C(5)-H(5)	0.9500
C(5A)-C(6)	1.399(4)
C(5A)-C(9A)	1.415(4)
C(6)-C(7)	1.385(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.408(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.392(4)
C(8)-H(8)	0.9500

C(9)-C(9A)	1.425(4)
C(9)-Mn	2.061(3)
C(9A)-C(9B)	1.428(4)
C(9B)-N	1.364(3)
C(10)-O(1)	1.153(3)
C(10)-Mn	1.839(3)
C(11)-O(2)	1.149(3)
C(11)-Mn	1.810(3)
C(12)-O(3)	1.136(4)
C(12)-Mn	1.860(4)
C(13)-O(4)	1.142(4)
C(13)-Mn	1.841(3)
Mn-N	2.073(2)
N-C(1)-C(2)	122.7(3)
N-C(1)-H(1)	118.6
C(2)-C(1)-H(1)	118.6
C(3)-C(2)-C(1)	120.0(2)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(2)-C(3)-C(3A)	119.2(2)
C(2)-C(3)-H(3)	120.4
C(3A)-C(3)-H(3)	120.4
C(9B)-C(3A)-C(3)	117.3(2)
C(9B)-C(3A)-C(4)	116.7(2)
C(3)-C(3A)-C(4)	126.0(2)
C(5)-C(4)-C(3A)	122.8(2)
C(5)-C(4)-Br	119.2(2)
C(3A)-C(4)-Br	118.09(19)
C(4)-C(5)-C(5A)	121.0(2)
C(4)-C(5)-H(5)	119.5

C(5A)-C(5)-H(5)	119.5
C(6)-C(5A)-C(9A)	118.3(2)
C(6)-C(5A)-C(5)	123.5(2)
C(9A)-C(5A)-C(5)	118.2(2)
C(7)-C(6)-C(5A)	119.4(3)
C(7)-C(6)-H(6)	120.3
C(5A)-C(6)-H(6)	120.3
C(6)-C(7)-C(8)	121.6(2)
C(6)-C(7)-H(7)	119.2
C(8)-C(7)-H(7)	119.2
C(9)-C(8)-C(7)	121.4(2)
C(9)-C(8)-H(8)	119.3
C(7)-C(8)-H(8)	119.3
C(8)-C(9)-C(9A)	116.0(2)
C(8)-C(9)-Mn	132.0(2)
C(9A)-C(9)-Mn	111.98(18)
C(5A)-C(9A)-C(9)	123.2(2)
C(5A)-C(9A)-C(9B)	119.5(2)
C(9)-C(9A)-C(9B)	117.3(2)
N-C(9B)-C(3A)	122.8(2)
N-C(9B)-C(9A)	115.4(2)
C(3A)-C(9B)-C(9A)	121.8(2)
O(1)-C(10)-Mn	179.7(3)
O(2)-C(11)-Mn	177.5(3)
O(3)-C(12)-Mn	175.7(2)
O(4)-C(13)-Mn	176.3(2)
C(11)-Mn-C(10)	93.01(12)
C(11)-Mn-C(13)	86.85(12)
C(10)-Mn-C(13)	97.06(13)
C(11)-Mn-C(12)	89.69(13)

C(10)-Mn-C(12)	94.39(13)
C(13)-Mn-C(12)	168.20(12)
C(11)-Mn-C(9)	93.78(11)
C(10)-Mn-C(9)	172.27(11)
C(13)-Mn-C(9)	87.00(11)
C(12)-Mn-C(9)	81.97(12)
C(11)-Mn-N	173.08(11)
C(10)-Mn-N	93.11(10)
C(13)-Mn-N	89.18(11)
C(12)-Mn-N	93.07(11)
C(9)-Mn-N	80.34(9)
C(1)-N-C(9B)	117.9(2)
C(1)-N-Mn	127.06(19)
C(9B)-N-Mn	114.99(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **32**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	22(1)	25(2)	33(2)	6(1)	8(1)	4(1)
C(2)	19(1)	34(2)	36(2)	10(1)	4(1)	9(1)
C(3)	29(1)	27(2)	33(2)	10(1)	8(1)	12(1)
C(3A)	27(1)	22(1)	23(2)	5(1)	10(1)	6(1)
C(4)	32(1)	17(1)	28(2)	7(1)	11(1)	11(1)
C(5)	30(1)	19(1)	25(2)	3(1)	10(1)	4(1)
C(5A)	26(1)	21(1)	23(2)	2(1)	10(1)	3(1)

C(6)	24(1)	24(2)	30(2)	-1(1)	7(1)	-2(1)
C(7)	19(1)	31(2)	32(2)	3(1)	4(1)	5(1)
C(8)	24(1)	24(1)	26(2)	5(1)	7(1)	7(1)
C(9)	21(1)	22(1)	23(2)	5(1)	9(1)	3(1)
C(9A)	21(1)	22(1)	20(1)	3(1)	9(1)	4(1)
C(9B)	22(1)	19(1)	22(2)	4(1)	10(1)	6(1)
C(10)	28(1)	27(2)	30(2)	8(1)	11(1)	12(1)
C(11)	26(1)	22(1)	23(2)	3(1)	6(1)	1(1)
C(12)	24(1)	21(1)	34(2)	8(1)	9(1)	6(1)
C(13)	17(1)	18(1)	27(2)	3(1)	1(1)	0(1)
Br	41(1)	21(1)	38(1)	6(1)	5(1)	12(1)
Mn	20(1)	19(1)	24(1)	6(1)	6(1)	4(1)
N	20(1)	21(1)	27(1)	7(1)	7(1)	3(1)
O(1)	26(1)	26(1)	44(1)	4(1)	11(1)	-3(1)
O(2)	33(1)	29(1)	35(1)	7(1)	2(1)	13(1)
O(3)	38(1)	36(1)	29(1)	5(1)	13(1)	6(1)
O(4)	26(1)	39(1)	27(1)	1(1)	9(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **32**.

	x	y	z	U(eq)
H(1)	-3615	1473	1199	32
H(2)	-5116	3105	312	35
H(3)	-3072	5124	616	34
H(5)	4215	6798	2688	29
H(6)	7286	5803	3866	32
H(7)	8431	4013	4611	34

H(8)	6071	2064	4251	29

Table 6. Torsion angles [deg] for **32**.

N-C(1)-C(2)-C(3)	-1.0(5)
C(1)-C(2)-C(3)-C(3A)	1.7(5)
C(2)-C(3)-C(3A)-C(9B)	-1.3(4)
C(2)-C(3)-C(3A)-C(4)	179.9(3)
C(9B)-C(3A)-C(4)-C(5)	1.4(4)
C(3)-C(3A)-C(4)-C(5)	-179.8(3)
C(9B)-C(3A)-C(4)-Br	-178.4(2)
C(3)-C(3A)-C(4)-Br	0.4(4)
C(3A)-C(4)-C(5)-C(5A)	0.1(5)
Br-C(4)-C(5)-C(5A)	179.9(2)
C(4)-C(5)-C(5A)-C(6)	179.5(3)
C(4)-C(5)-C(5A)-C(9A)	-0.7(4)
C(9A)-C(5A)-C(6)-C(7)	-0.3(4)
C(5)-C(5A)-C(6)-C(7)	179.4(3)
C(5A)-C(6)-C(7)-C(8)	0.2(5)
C(6)-C(7)-C(8)-C(9)	0.5(5)
C(7)-C(8)-C(9)-C(9A)	-1.0(4)
C(7)-C(8)-C(9)-Mn	-178.3(2)
C(6)-C(5A)-C(9A)-C(9)	-0.2(4)
C(5)-C(5A)-C(9A)-C(9)	-179.9(3)
C(6)-C(5A)-C(9A)-C(9B)	179.6(3)
C(5)-C(5A)-C(9A)-C(9B)	-0.2(4)
C(8)-C(9)-C(9A)-C(5A)	0.8(4)
Mn-C(9)-C(9A)-C(5A)	178.7(2)
C(8)-C(9)-C(9A)-C(9B)	-178.9(3)

Mn-C(9)-C(9A)-C(9B)	-1.1(3)
C(3)-C(3A)-C(9B)-N	0.0(4)
C(4)-C(3A)-C(9B)-N	179.0(3)
C(3)-C(3A)-C(9B)-C(9A)	178.8(3)
C(4)-C(3A)-C(9B)-C(9A)	-2.3(4)
C(5A)-C(9A)-C(9B)-N	-179.4(3)
C(9)-C(9A)-C(9B)-N	0.3(4)
C(5A)-C(9A)-C(9B)-C(3A)	1.7(4)
C(9)-C(9A)-C(9B)-C(3A)	-178.5(3)
O(2)-C(11)-Mn-C(10)	114(6)
O(2)-C(11)-Mn-C(13)	17(6)
O(2)-C(11)-Mn-C(12)	-151(6)
O(2)-C(11)-Mn-C(9)	-69(6)
O(2)-C(11)-Mn-N	-38(7)
O(1)-C(10)-Mn-C(11)	49(58)
O(1)-C(10)-Mn-C(13)	137(57)
O(1)-C(10)-Mn-C(12)	-41(58)
O(1)-C(10)-Mn-C(9)	-102(57)
O(1)-C(10)-Mn-N	-134(57)
O(4)-C(13)-Mn-C(11)	-35(4)
O(4)-C(13)-Mn-C(10)	-127(4)
O(4)-C(13)-Mn-C(12)	38(4)
O(4)-C(13)-Mn-C(9)	59(4)
O(4)-C(13)-Mn-N	140(4)
O(3)-C(12)-Mn-C(11)	47(3)
O(3)-C(12)-Mn-C(10)	140(3)
O(3)-C(12)-Mn-C(13)	-25(4)
O(3)-C(12)-Mn-C(9)	-46(3)
O(3)-C(12)-Mn-N	-126(3)
C(8)-C(9)-Mn-C(11)	-5.2(3)

C(9A)-C(9)-Mn-C(11)	177.4(2)
C(8)-C(9)-Mn-C(10)	146.2(8)
C(9A)-C(9)-Mn-C(10)	-31.2(10)
C(8)-C(9)-Mn-C(13)	-91.9(3)
C(9A)-C(9)-Mn-C(13)	90.7(2)
C(8)-C(9)-Mn-C(12)	83.9(3)
C(9A)-C(9)-Mn-C(12)	-93.5(2)
C(8)-C(9)-Mn-N	178.5(3)
C(9A)-C(9)-Mn-N	1.0(2)
C(2)-C(1)-N-C(9B)	-0.3(4)
C(2)-C(1)-N-Mn	-178.8(2)
C(3A)-C(9B)-N-C(1)	0.7(4)
C(9A)-C(9B)-N-C(1)	-178.1(3)
C(3A)-C(9B)-N-Mn	179.4(2)
C(9A)-C(9B)-N-Mn	0.6(3)
C(11)-Mn-N-C(1)	145.5(9)
C(10)-Mn-N-C(1)	-6.5(3)
C(13)-Mn-N-C(1)	90.5(3)
C(12)-Mn-N-C(1)	-101.1(3)
C(9)-Mn-N-C(1)	177.6(3)
C(11)-Mn-N-C(9B)	-33.0(11)
C(10)-Mn-N-C(9B)	175.0(2)
C(13)-Mn-N-C(9B)	-88.0(2)
C(12)-Mn-N-C(9B)	80.4(2)
C(9)-Mn-N-C(9B)	-0.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **32** [A and deg.].

D-H...A d(D-H) d(H...A) d(D...A) <(DHA)

2.16 Tetracarbonyl{pentacarbonyl[benzo[*h*]quinoline-κC^9-κ*N*-4-(methoxy)carbene]chromium(0)}manganese(I) (33)

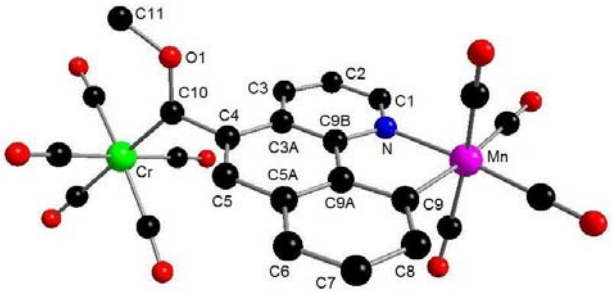


Table 1. Crystal data and structure refinement for **33**.

Empirical formula	C24 H10 Cr Mn N O10
Formula weight	579.27
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 6.66030(10) A alpha = 90 deg.
	b = 12.9097(2) A beta = 96.4883(9) deg.
	c = 26.8855(5) A gamma = 90 deg.
Volume	2296.87(7) A^3
Z, Calculated density	4, 1.675 Mg/m^3
Absorption coefficient	1.084 mm^-1
F(000)	1160
Crystal size	0.56 x 0.16 x 0.12 mm
Theta range for data collection	2.78 to 30.00 deg.
Limiting indices	-9<=h<=6, -18<=k<=17, -37<=l<=36
Reflections collected / unique	26444 / 6649 [R(int) = 0.1067]
Completeness to theta = 30.00	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8809 and 0.5819

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6649 / 0 / 335
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1320
R indices (all data)	R1 = 0.0737, wR2 = 0.1403
Largest diff. peak and hole	1.551 and -1.112 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **33**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3218(4)	8361(2)	1170(1)	19(1)
C(2)	4003(4)	9169(2)	906(1)	21(1)
C(3)	3113(4)	10132(2)	907(1)	19(1)
C(3A)	1418(4)	10276(2)	1162(1)	16(1)
C(4)	328(4)	11245(2)	1183(1)	17(1)
C(5)	-1367(4)	11298(2)	1423(1)	18(1)
C(5A)	-2093(4)	10428(2)	1683(1)	17(1)
C(6)	-3773(4)	10479(2)	1957(1)	20(1)
C(7)	-4340(4)	9612(2)	2207(1)	22(1)
C(8)	-3271(4)	8667(2)	2189(1)	21(1)
C(9)	-1614(4)	8578(2)	1928(1)	18(1)
C(9A)	-1047(4)	9481(2)	1676(1)	15(1)
C(9B)	691(4)	9416(2)	1411(1)	16(1)
C(10)	1148(4)	12222(2)	980(1)	18(1)
C(11)	3775(5)	13443(2)	1277(1)	32(1)
C(12)	-1330(4)	13546(2)	-250(1)	24(1)
C(13)	-933(4)	13987(2)	741(1)	25(1)

C(14)	2348(4)	13618(2)	201(1)	24(1)
C(15)	819(4)	11744(2)	-30(1)	22(1)
C(16)	-2554(4)	12182(2)	353(1)	23(1)
C(17)	-1013(4)	6495(2)	2220(1)	24(1)
C(18)	2272(4)	6385(2)	1758(1)	24(1)
C(19)	-1481(4)	7047(2)	1290(1)	21(1)
C(20)	1596(4)	7905(2)	2434(1)	21(1)
Cr	-62(1)	12894(1)	337(1)	17(1)
Mn	329(1)	7364(1)	1847(1)	17(1)
N	1618(3)	8470(2)	1423(1)	17(1)
O(1)	2662(3)	12483(1)	1314(1)	25(1)
O(2)	-2094(4)	13952(2)	-599(1)	33(1)
O(3)	-1486(4)	14603(2)	998(1)	41(1)
O(4)	3686(3)	14047(2)	79(1)	35(1)
O(5)	1325(3)	11057(2)	-253(1)	32(1)
O(6)	-4077(3)	11786(2)	319(1)	33(1)
O(7)	-1877(4)	5960(2)	2459(1)	40(1)
O(8)	3493(4)	5779(2)	1717(1)	36(1)
O(9)	-2677(3)	6914(2)	962(1)	30(1)
O(10)	2234(3)	8259(2)	2805(1)	32(1)

Table 3. Bond lengths [A] and angles [deg] for **33**.

C(1)-N	1.334(3)
C(1)-C(2)	1.397(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.377(3)
C(2)-H(2A)	0.9500
C(3)-C(3A)	1.398(3)

C(3)-H(3A)	0.9500
C(3A)-C(9B)	1.410(3)
C(3A)-C(4)	1.451(3)
C(4)-C(5)	1.365(3)
C(4)-C(10)	1.501(3)
C(5)-C(5A)	1.434(3)
C(5)-H(5A)	0.9500
C(5A)-C(6)	1.409(3)
C(5A)-C(9A)	1.409(3)
C(6)-C(7)	1.379(3)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.416(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.379(3)
C(8)-H(8A)	0.9500
C(9)-C(9A)	1.420(3)
C(9)-Mn	2.059(2)
C(9A)-C(9B)	1.429(3)
C(9B)-N	1.367(3)
C(10)-O(1)	1.316(3)
C(10)-Cr	2.019(2)
C(11)-O(1)	1.454(3)
C(11)-H(11C)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11A)	0.9800
C(12)-O(2)	1.143(3)
C(12)-Cr	1.900(3)
C(13)-O(3)	1.142(3)
C(13)-Cr	1.911(3)
C(14)-O(4)	1.129(3)

C(14)-Cr	1.928(3)
C(15)-O(5)	1.143(3)
C(15)-Cr	1.911(3)
C(16)-O(6)	1.131(3)
C(16)-Cr	1.902(3)
C(17)-O(7)	1.142(3)
C(17)-Mn	1.807(3)
C(18)-O(8)	1.142(3)
C(18)-Mn	1.844(3)
C(19)-O(9)	1.134(3)
C(19)-Mn	1.859(3)
C(20)-O(10)	1.136(3)
C(20)-Mn	1.841(3)
Mn-N	2.073(2)
N-C(1)-C(2)	123.1(2)
N-C(1)-H(1A)	118.4
C(2)-C(1)-H(1A)	118.4
C(3)-C(2)-C(1)	119.2(2)
C(3)-C(2)-H(2A)	120.4
C(1)-C(2)-H(2A)	120.4
C(2)-C(3)-C(3A)	119.5(2)
C(2)-C(3)-H(3A)	120.2
C(3A)-C(3)-H(3A)	120.2
C(3)-C(3A)-C(9B)	117.9(2)
C(3)-C(3A)-C(4)	124.7(2)
C(9B)-C(3A)-C(4)	117.4(2)
C(5)-C(4)-C(3A)	120.4(2)
C(5)-C(4)-C(10)	119.0(2)
C(3A)-C(4)-C(10)	120.4(2)
C(4)-C(5)-C(5A)	122.2(2)

C(4)-C(5)-H(5A) 118.9

C(5A)-C(5)-H(5A) 118.9

C(6)-C(5A)-C(9A) 118.0(2)

C(6)-C(5A)-C(5) 123.3(2)

C(9A)-C(5A)-C(5) 118.6(2)

C(7)-C(6)-C(5A) 119.6(2)

C(7)-C(6)-H(6A) 120.2

C(5A)-C(6)-H(6A) 120.2

C(6)-C(7)-C(8) 121.1(2)

C(6)-C(7)-H(7A) 119.4

C(8)-C(7)-H(7A) 119.4

C(9)-C(8)-C(7) 121.5(2)

C(9)-C(8)-H(8A) 119.3

C(7)-C(8)-H(8A) 119.3

C(8)-C(9)-C(9A) 116.5(2)

C(8)-C(9)-Mn 131.70(18)

C(9A)-C(9)-Mn 111.77(17)

C(5A)-C(9A)-C(9) 123.3(2)

C(5A)-C(9A)-C(9B) 119.2(2)

C(9)-C(9A)-C(9B) 117.6(2)

N-C(9B)-C(3A) 122.4(2)

N-C(9B)-C(9A) 115.5(2)

C(3A)-C(9B)-C(9A) 122.1(2)

O(1)-C(10)-C(4) 104.44(19)

O(1)-C(10)-Cr 132.44(17)

C(4)-C(10)-Cr 123.10(17)

O(1)-C(11)-H(11C) 109.5

O(1)-C(11)-H(11B) 109.5

H(11C)-C(11)-H(11B) 109.5

O(1)-C(11)-H(11A) 109.5

H(11C)-C(11)-H(11A)	109.5
H(11B)-C(11)-H(11A)	109.5
O(2)-C(12)-Cr	179.0(2)
O(3)-C(13)-Cr	176.6(2)
O(4)-C(14)-Cr	173.9(2)
O(5)-C(15)-Cr	179.2(2)
O(6)-C(16)-Cr	173.8(2)
O(7)-C(17)-Mn	178.8(3)
O(8)-C(18)-Mn	178.1(2)
O(9)-C(19)-Mn	174.6(2)
O(10)-C(20)-Mn	174.7(2)
C(12)-Cr-C(16)	85.79(11)
C(12)-Cr-C(13)	90.60(11)
C(16)-Cr-C(13)	91.24(12)
C(12)-Cr-C(15)	92.82(11)
C(16)-Cr-C(15)	87.51(11)
C(13)-Cr-C(15)	176.26(10)
C(12)-Cr-C(14)	85.92(11)
C(16)-Cr-C(14)	170.45(11)
C(13)-Cr-C(14)	93.58(12)
C(15)-Cr-C(14)	88.17(11)
C(12)-Cr-C(10)	176.79(11)
C(16)-Cr-C(10)	92.13(10)
C(13)-Cr-C(10)	87.00(10)
C(15)-Cr-C(10)	89.53(10)
C(14)-Cr-C(10)	96.35(11)
C(17)-Mn-C(18)	92.55(12)
C(17)-Mn-C(20)	88.14(11)
C(18)-Mn-C(20)	96.36(12)
C(17)-Mn-C(19)	89.67(11)

C(18)-Mn-C(19)	98.35(11)
C(20)-Mn-C(19)	165.21(11)
C(17)-Mn-C(9)	93.33(11)
C(18)-Mn-C(9)	173.70(11)
C(20)-Mn-C(9)	81.60(10)
C(19)-Mn-C(9)	83.93(10)
C(17)-Mn-N	173.95(10)
C(18)-Mn-N	93.47(10)
C(20)-Mn-N	91.83(9)
C(19)-Mn-N	88.83(9)
C(9)-Mn-N	80.68(9)
C(1)-N-C(9B)	117.8(2)
C(1)-N-Mn	127.74(16)
C(9B)-N-Mn	114.43(16)
C(10)-O(1)-C(11)	121.98(19)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **33**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	12(1)	21(1)	25(1)	-2(1)	4(1)	2(1)
C(2)	12(1)	25(1)	25(1)	-2(1)	6(1)	-1(1)
C(3)	12(1)	22(1)	23(1)	2(1)	3(1)	-3(1)
C(3A)	12(1)	17(1)	20(1)	0(1)	3(1)	-1(1)
C(4)	14(1)	17(1)	21(1)	0(1)	2(1)	0(1)
C(5)	16(1)	17(1)	22(1)	-1(1)	3(1)	1(1)

C(5A)	10(1)	19(1)	20(1)	-1(1)	2(1)	0(1)
C(6)	14(1)	22(1)	25(1)	-2(1)	5(1)	2(1)
C(7)	14(1)	28(1)	25(1)	-2(1)	7(1)	0(1)
C(8)	16(1)	23(1)	24(1)	3(1)	6(1)	-3(1)
C(9)	14(1)	20(1)	19(1)	-1(1)	3(1)	0(1)
C(9A)	10(1)	19(1)	17(1)	-2(1)	2(1)	0(1)
C(9B)	10(1)	18(1)	19(1)	-1(1)	2(1)	-1(1)
C(10)	13(1)	18(1)	23(1)	-1(1)	5(1)	1(1)
C(11)	27(2)	27(1)	40(2)	4(1)	-7(1)	-13(1)
C(12)	23(1)	22(1)	27(1)	1(1)	5(1)	-4(1)
C(13)	22(1)	23(1)	31(1)	4(1)	4(1)	0(1)
C(14)	19(1)	24(1)	30(1)	1(1)	5(1)	-4(1)
C(15)	14(1)	27(1)	25(1)	2(1)	1(1)	-4(1)
C(16)	18(1)	27(1)	23(1)	3(1)	3(1)	-2(1)
C(17)	18(1)	24(1)	30(1)	5(1)	-1(1)	-2(1)
C(18)	22(1)	22(1)	26(1)	4(1)	3(1)	2(1)
C(19)	18(1)	18(1)	30(1)	0(1)	8(1)	1(1)
C(20)	18(1)	21(1)	25(1)	8(1)	6(1)	-1(1)
Cr	13(1)	17(1)	23(1)	2(1)	4(1)	-2(1)
Mn	12(1)	17(1)	23(1)	2(1)	3(1)	0(1)
N	11(1)	18(1)	22(1)	1(1)	4(1)	1(1)
O(1)	21(1)	22(1)	30(1)	3(1)	-4(1)	-6(1)
O(2)	37(1)	33(1)	29(1)	5(1)	0(1)	3(1)
O(3)	41(1)	31(1)	54(1)	-9(1)	14(1)	4(1)
O(4)	28(1)	36(1)	43(1)	-2(1)	12(1)	-14(1)
O(5)	28(1)	32(1)	36(1)	-8(1)	5(1)	2(1)
O(6)	20(1)	42(1)	37(1)	7(1)	4(1)	-10(1)
O(7)	30(1)	42(1)	47(1)	17(1)	4(1)	-13(1)
O(8)	37(1)	33(1)	37(1)	4(1)	5(1)	19(1)
O(9)	23(1)	33(1)	33(1)	-6(1)	-2(1)	2(1)

O(10)	31(1)	37(1)	28(1)	3(1)	0(1)	-12(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **33**.

	x	y	z	U(eq)
H(1A)	3855	7702	1170	23
H(2A)	5135	9056	727	25
H(3A)	3648	10694	736	23
H(5A)	-2090	11933	1419	22
H(6A)	-4511	11106	1969	24
H(7A)	-5466	9650	2393	26
H(8A)	-3706	8080	2362	25
H(11C)	4454	13629	1608	49
H(11B)	2837	13997	1156	49
H(11A)	4785	13352	1043	49

Table 6. Torsion angles [deg] for **33**.

N-C(1)-C(2)-C(3)	0.8(4)
C(1)-C(2)-C(3)-C(3A)	-1.5(4)
C(2)-C(3)-C(3A)-C(9B)	0.2(3)
C(2)-C(3)-C(3A)-C(4)	-178.8(2)
C(3)-C(3A)-C(4)-C(5)	177.1(2)
C(9B)-C(3A)-C(4)-C(5)	-1.8(3)
C(3)-C(3A)-C(4)-C(10)	-8.3(4)
C(9B)-C(3A)-C(4)-C(10)	172.7(2)
C(3A)-C(4)-C(5)-C(5A)	2.8(4)

C(10)-C(4)-C(5)-C(5A)	-171.9(2)
C(4)-C(5)-C(5A)-C(6)	176.4(2)
C(4)-C(5)-C(5A)-C(9A)	-1.7(3)
C(9A)-C(5A)-C(6)-C(7)	-0.1(3)
C(5)-C(5A)-C(6)-C(7)	-178.2(2)
C(5A)-C(6)-C(7)-C(8)	-0.5(4)
C(6)-C(7)-C(8)-C(9)	0.7(4)
C(7)-C(8)-C(9)-C(9A)	-0.2(4)
C(7)-C(8)-C(9)-Mn	177.19(18)
C(6)-C(5A)-C(9A)-C(9)	0.6(3)
C(5)-C(5A)-C(9A)-C(9)	178.8(2)
C(6)-C(5A)-C(9A)-C(9B)	-178.5(2)
C(5)-C(5A)-C(9A)-C(9B)	-0.2(3)
C(8)-C(9)-C(9A)-C(5A)	-0.4(3)
Mn-C(9)-C(9A)-C(5A)	-178.34(18)
C(8)-C(9)-C(9A)-C(9B)	178.7(2)
Mn-C(9)-C(9A)-C(9B)	0.8(3)
C(3)-C(3A)-C(9B)-N	2.0(3)
C(4)-C(3A)-C(9B)-N	-178.9(2)
C(3)-C(3A)-C(9B)-C(9A)	-179.1(2)
C(4)-C(3A)-C(9B)-C(9A)	-0.1(3)
C(5A)-C(9A)-C(9B)-N	-180.0(2)
C(9)-C(9A)-C(9B)-N	0.9(3)
C(5A)-C(9A)-C(9B)-C(3A)	1.1(3)
C(9)-C(9A)-C(9B)-C(3A)	-178.0(2)
C(5)-C(4)-C(10)-O(1)	100.4(3)
C(3A)-C(4)-C(10)-O(1)	-74.2(3)
C(5)-C(4)-C(10)-Cr	-78.1(3)
C(3A)-C(4)-C(10)-Cr	107.3(2)
O(2)-C(12)-Cr-C(16)	108(14)

O(2)-C(12)-Cr-C(13)	17(14)
O(2)-C(12)-Cr-C(15)	-165(14)
O(2)-C(12)-Cr-C(14)	-77(14)
O(2)-C(12)-Cr-C(10)	58(15)
O(6)-C(16)-Cr-C(12)	17(2)
O(6)-C(16)-Cr-C(13)	107(2)
O(6)-C(16)-Cr-C(15)	-76(2)
O(6)-C(16)-Cr-C(14)	-13(3)
O(6)-C(16)-Cr-C(10)	-166(2)
O(3)-C(13)-Cr-C(12)	132(4)
O(3)-C(13)-Cr-C(16)	46(4)
O(3)-C(13)-Cr-C(15)	-24(6)
O(3)-C(13)-Cr-C(14)	-142(4)
O(3)-C(13)-Cr-C(10)	-46(4)
O(5)-C(15)-Cr-C(12)	-36(18)
O(5)-C(15)-Cr-C(16)	49(18)
O(5)-C(15)-Cr-C(13)	120(17)
O(5)-C(15)-Cr-C(14)	-122(18)
O(5)-C(15)-Cr-C(10)	142(18)
O(4)-C(14)-Cr-C(12)	-23(2)
O(4)-C(14)-Cr-C(16)	7(3)
O(4)-C(14)-Cr-C(13)	-113(2)
O(4)-C(14)-Cr-C(15)	70(2)
O(4)-C(14)-Cr-C(10)	159(2)
O(1)-C(10)-Cr-C(12)	-108.9(18)
C(4)-C(10)-Cr-C(12)	69.1(18)
O(1)-C(10)-Cr-C(16)	-158.4(2)
C(4)-C(10)-Cr-C(16)	19.6(2)
O(1)-C(10)-Cr-C(13)	-67.3(2)
C(4)-C(10)-Cr-C(13)	110.7(2)

O(1)-C(10)-Cr-C(15)	114.1(2)
C(4)-C(10)-Cr-C(15)	-67.9(2)
O(1)-C(10)-Cr-C(14)	26.0(3)
C(4)-C(10)-Cr-C(14)	-156.0(2)
O(7)-C(17)-Mn-C(18)	162(100)
O(7)-C(17)-Mn-C(20)	65(13)
O(7)-C(17)-Mn-C(19)	-100(13)
O(7)-C(17)-Mn-C(9)	-16(13)
O(7)-C(17)-Mn-N	-24(13)
O(8)-C(18)-Mn-C(17)	-67(8)
O(8)-C(18)-Mn-C(20)	22(8)
O(8)-C(18)-Mn-C(19)	-157(8)
O(8)-C(18)-Mn-C(9)	92(8)
O(8)-C(18)-Mn-N	114(8)
O(10)-C(20)-Mn-C(17)	-60(2)
O(10)-C(20)-Mn-C(18)	-152(2)
O(10)-C(20)-Mn-C(19)	22(3)
O(10)-C(20)-Mn-C(9)	34(2)
O(10)-C(20)-Mn-N	114(2)
O(9)-C(19)-Mn-C(17)	88(2)
O(9)-C(19)-Mn-C(18)	-180(100)
O(9)-C(19)-Mn-C(20)	6(3)
O(9)-C(19)-Mn-C(9)	-6(2)
O(9)-C(19)-Mn-N	-87(2)
C(8)-C(9)-Mn-C(17)	2.0(2)
C(9A)-C(9)-Mn-C(17)	179.47(17)
C(8)-C(9)-Mn-C(18)	-157.1(9)
C(9A)-C(9)-Mn-C(18)	20.4(10)
C(8)-C(9)-Mn-C(20)	-85.7(2)
C(9A)-C(9)-Mn-C(20)	91.85(17)

C(8)-C(9)-Mn-C(19)	91.3(2)
C(9A)-C(9)-Mn-C(19)	-91.22(17)
C(8)-C(9)-Mn-N	-178.9(2)
C(9A)-C(9)-Mn-N	-1.42(16)
C(2)-C(1)-N-C(9B)	1.3(3)
C(2)-C(1)-N-Mn	-178.15(17)
C(3A)-C(9B)-N-C(1)	-2.7(3)
C(9A)-C(9B)-N-C(1)	178.3(2)
C(3A)-C(9B)-N-Mn	176.79(17)
C(9A)-C(9B)-N-Mn	-2.1(2)
C(17)-Mn-N-C(1)	-170.2(9)
C(18)-Mn-N-C(1)	3.8(2)
C(20)-Mn-N-C(1)	100.3(2)
C(19)-Mn-N-C(1)	-94.5(2)
C(9)-Mn-N-C(1)	-178.5(2)
C(17)-Mn-N-C(9B)	10.4(10)
C(18)-Mn-N-C(9B)	-175.69(17)
C(20)-Mn-N-C(9B)	-79.21(17)
C(19)-Mn-N-C(9B)	86.01(17)
C(9)-Mn-N-C(9B)	1.97(16)
C(4)-C(10)-O(1)-C(11)	-175.0(2)
Cr-C(10)-O(1)-C(11)	3.3(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **33** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.17 Tetracarbonyl{tricarbonyl(η^6-3b,4,5,6,7,7a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline-κC^{11}-κN)chromium(0)}manganese(I) (34)

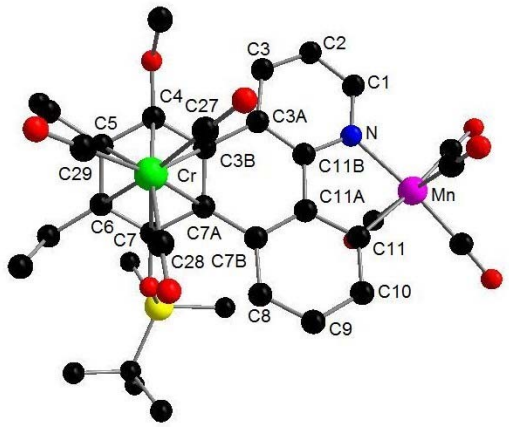


Table 1. Crystal data and structure refinement for **34**.

Empirical formula	C36 H36 Cl2 Cr Mn N O9 Si
Formula weight	832.59
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P222
Unit cell dimensions	a = 13.0742(2) A alpha = 90 deg. b = 21.2949(4) A beta = 90 deg. c = 27.0004(5) A gamma = 90 deg.
Volume	7517.3(2) A^3
Z, Calculated density	8, 1.471 Mg/m^3
Absorption coefficient	0.853 mm^-1
F(000)	3424
Crystal size	0.24 x 0.23 x 0.10 mm
Theta range for data collection	1.91 to 27.49 deg.
Limiting indices	-16<=h<=16, -27<=k<=27, -35<=l<=32
Reflections collected / unique	46089 / 8569 [R(int) = 0.0525]
Completeness to theta = 27.49	99.5 %
Absorption correction	Analytical
Max. and min. transmission	0.9196 and 0.8241
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8569 / 0 / 479
Goodness-of-fit on F^2	1.008

Final R indices [I>2sigma(I)] R1 = 0.0365, wR2 = 0.0955

R indices (all data) R1 = 0.0615, wR2 = 0.1041

Largest diff. peak and hole 0.594 and -0.515 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **34**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mn(1)	7180(1)	6164(1)	5529(1)	18(1)
Cr(1)	6417(1)	8275(1)	3629(1)	15(1)
Si(1)	8172(1)	6430(1)	2917(1)	17(1)
N(1)	7740(1)	7038(1)	5336(1)	18(1)
O(1)	8365(1)	9006(1)	4170(1)	20(1)
O(2)	7243(1)	6979(1)	3015(1)	15(1)
O(3)	5308(1)	6805(1)	5919(1)	35(1)
O(4)	8311(1)	6053(1)	6483(1)	32(1)
O(5)	6287(1)	4908(1)	5679(1)	40(1)
O(6)	8773(1)	5495(1)	4931(1)	30(1)
O(7)	5167(1)	8607(1)	4521(1)	40(1)
O(8)	4563(1)	7583(1)	3283(1)	28(1)
O(9)	5548(1)	9422(1)	3141(1)	33(1)
C(1)	8268(2)	7423(1)	5632(1)	23(1)
C(2)	8654(2)	7990(1)	5469(1)	26(1)
C(3)	8475(2)	8178(1)	4989(1)	23(1)
C(3A)	7889(2)	7798(1)	4672(1)	16(1)
C(3B)	7714(1)	7927(1)	4138(1)	15(1)
C(4)	7985(2)	8505(1)	3903(1)	16(1)
C(5)	7948(2)	8579(1)	3382(1)	16(1)
C(6)	7695(2)	8055(1)	3078(1)	16(1)
C(7)	7417(2)	7487(1)	3310(1)	15(1)
C(7A)	7302(1)	7430(1)	3836(1)	14(1)
C(7B)	6790(2)	6890(1)	4070(1)	14(1)
C(8)	6109(2)	6484(1)	3825(1)	15(1)
C(9)	5665(2)	5994(1)	4076(1)	17(1)
C(10)	5894(2)	5872(1)	4573(1)	18(1)
C(11)	6553(2)	6258(1)	4837(1)	16(1)
C(11A)	6955(2)	6784(1)	4577(1)	14(1)
C(11B)	7554(2)	7221(1)	4861(1)	15(1)
C(12)	7618(2)	9406(1)	4401(1)	28(1)
C(13)	8277(2)	9195(1)	3158(1)	21(1)
C(14)	9442(2)	9210(1)	3074(1)	34(1)
C(15)	7743(2)	8081(1)	2519(1)	20(1)
C(16)	6704(2)	8170(1)	2269(1)	34(1)
C(17)	7744(2)	6023(1)	2333(1)	22(1)
C(18)	7583(2)	6484(1)	1906(1)	31(1)
C(19)	6728(2)	5684(1)	2439(1)	30(1)
C(20)	8558(2)	5535(1)	2187(1)	42(1)
C(21)	9427(2)	6837(1)	2866(1)	26(1)
C(22)	8248(2)	5873(1)	3446(1)	26(1)
C(23)	6022(2)	6562(1)	5777(1)	24(1)
C(24)	7882(2)	6114(1)	6121(1)	21(1)
C(25)	6622(2)	5405(1)	5627(1)	26(1)

C(26)	8204(2)	5768(1)	5170(1)	21(1)
C(27)	5664(2)	8482(1)	4176(1)	23(1)
C(28)	5286(2)	7850(1)	3411(1)	18(1)
C(29)	5889(2)	8977(1)	3328(1)	22(1)
C(30)	11057(2)	5955(1)	4392(1)	40(1)
Cl(1)	10777(1)	5368(1)	3959(1)	41(1)
Cl(2)	10565(1)	6691(1)	4221(1)	61(1)

Table 3. Bond lengths [A] and angles [deg] for **34**.

Mn(1)-C(25)	1.795(3)
Mn(1)-C(24)	1.847(2)
Mn(1)-C(26)	1.855(3)
Mn(1)-C(23)	1.859(3)
Mn(1)-C(11)	2.050(2)
Mn(1)-N(1)	2.0654(19)
Cr(1)-C(27)	1.827(2)
Cr(1)-C(28)	1.831(2)
Cr(1)-C(29)	1.837(2)
Cr(1)-C(5)	2.207(2)
Cr(1)-C(7A)	2.211(2)
Cr(1)-C(4)	2.233(2)
Cr(1)-C(6)	2.286(2)
Cr(1)-C(7)	2.296(2)
Cr(1)-C(3B)	2.305(2)
Si(1)-O(2)	1.7069(15)
Si(1)-C(22)	1.857(2)
Si(1)-C(21)	1.862(2)
Si(1)-C(17)	1.883(2)
N(1)-C(1)	1.338(3)
N(1)-C(11B)	1.363(3)
O(1)-C(4)	1.381(3)
O(1)-C(12)	1.439(3)
O(2)-C(7)	1.360(2)
O(3)-C(23)	1.136(3)
O(4)-C(24)	1.135(3)
O(5)-C(25)	1.154(3)
O(6)-C(26)	1.144(3)
O(7)-C(27)	1.166(3)
O(8)-C(28)	1.157(3)
O(9)-C(29)	1.163(3)
C(1)-C(2)	1.382(3)
C(1)-H(1)	0.9500
C(2)-C(3)	1.377(3)
C(2)-H(2)	0.9500
C(3)-C(3A)	1.405(3)
C(3)-H(3)	0.9500
C(3A)-C(11B)	1.399(3)
C(3A)-C(3B)	1.487(3)
C(3B)-C(4)	1.429(3)
C(3B)-C(7A)	1.440(3)
C(4)-C(5)	1.416(3)
C(5)-C(6)	1.424(3)
C(5)-C(13)	1.507(3)
C(6)-C(7)	1.411(3)
C(6)-C(15)	1.513(3)
C(7)-C(7A)	1.434(3)

C(7A)-C(7B)	1.473(3)
C(7B)-C(11A)	1.403(3)
C(7B)-C(8)	1.407(3)
C(8)-C(9)	1.373(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.398(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.387(3)
C(10)-H(10)	0.9500
C(11)-C(11A)	1.423(3)
C(11A)-C(11B)	1.438(3)
C(12)-H(12A)	1.00(3)
C(12)-H(12B)	0.97(3)
C(12)-H(12C)	1.02(3)
C(13)-C(14)	1.540(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(14)-H(14D)	0.9800
C(14)-H(14E)	0.9800
C(14)-H(14F)	0.9800
C(15)-C(16)	1.528(3)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(16)-H(16D)	0.9800
C(16)-H(16E)	0.9800
C(16)-H(16F)	0.9800
C(17)-C(18)	1.530(3)
C(17)-C(19)	1.539(3)
C(17)-C(20)	1.540(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(18)-H(18D)	0.9800
C(18)-H(18E)	0.9800
C(18)-H(18F)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(19)-H(19D)	0.9800
C(19)-H(19E)	0.9800
C(19)-H(19F)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(20)-H(20D)	0.9800
C(20)-H(20E)	0.9800
C(20)-H(20F)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(21)-H(21D)	0.9800
C(21)-H(21E)	0.9800
C(21)-H(21F)	0.9800
C(22)-H(22A)	0.9800

C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(22)-H(22D)	0.9800
C(22)-H(22E)	0.9800
C(22)-H(22F)	0.9800
C(30)-Cl(1)	1.748(3)
C(30)-Cl(2)	1.757(3)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(25)-Mn(1)-C(24)	91.17(10)
C(25)-Mn(1)-C(26)	87.75(10)
C(24)-Mn(1)-C(26)	93.85(10)
C(25)-Mn(1)-C(23)	91.46(11)
C(24)-Mn(1)-C(23)	96.83(10)
C(26)-Mn(1)-C(23)	169.30(10)
C(25)-Mn(1)-C(11)	93.45(10)
C(24)-Mn(1)-C(11)	173.51(9)
C(26)-Mn(1)-C(11)	81.80(9)
C(23)-Mn(1)-C(11)	87.60(9)
C(25)-Mn(1)-N(1)	173.37(9)
C(24)-Mn(1)-N(1)	95.44(9)
C(26)-Mn(1)-N(1)	91.29(9)
C(23)-Mn(1)-N(1)	88.27(9)
C(11)-Mn(1)-N(1)	79.92(8)
C(27)-Cr(1)-C(28)	86.79(10)
C(27)-Cr(1)-C(29)	87.68(11)
C(28)-Cr(1)-C(29)	87.53(10)
C(27)-Cr(1)-C(5)	131.49(9)
C(28)-Cr(1)-C(5)	141.23(9)
C(29)-Cr(1)-C(5)	88.17(9)
C(27)-Cr(1)-C(7A)	105.88(9)
C(28)-Cr(1)-C(7A)	95.81(9)
C(29)-Cr(1)-C(7A)	166.17(9)
C(5)-Cr(1)-C(7A)	80.82(8)
C(27)-Cr(1)-C(4)	100.07(9)
C(28)-Cr(1)-C(4)	162.90(9)
C(29)-Cr(1)-C(4)	108.25(9)
C(5)-Cr(1)-C(4)	37.20(8)
C(7A)-Cr(1)-C(4)	67.30(8)
C(27)-Cr(1)-C(6)	165.63(9)
C(28)-Cr(1)-C(6)	106.20(9)
C(29)-Cr(1)-C(6)	98.80(9)
C(5)-Cr(1)-C(6)	36.89(8)
C(7A)-Cr(1)-C(6)	67.37(8)
C(4)-Cr(1)-C(6)	65.75(8)
C(27)-Cr(1)-C(7)	141.80(9)
C(28)-Cr(1)-C(7)	88.67(8)
C(29)-Cr(1)-C(7)	130.00(9)
C(5)-Cr(1)-C(7)	65.44(8)
C(7A)-Cr(1)-C(7)	37.05(7)
C(4)-Cr(1)-C(7)	76.22(7)
C(6)-Cr(1)-C(7)	35.85(7)
C(27)-Cr(1)-C(3B)	89.56(9)
C(28)-Cr(1)-C(3B)	128.81(9)
C(29)-Cr(1)-C(3B)	143.34(9)
C(5)-Cr(1)-C(3B)	66.89(7)
C(7A)-Cr(1)-C(3B)	37.12(8)
C(4)-Cr(1)-C(3B)	36.67(8)
C(6)-Cr(1)-C(3B)	77.56(7)
C(7)-Cr(1)-C(3B)	64.53(7)

O(2)-Si(1)-C(22)	110.86(9)
O(2)-Si(1)-C(21)	108.61(9)
C(22)-Si(1)-C(21)	107.85(11)
O(2)-Si(1)-C(17)	103.52(9)
C(22)-Si(1)-C(17)	111.47(11)
C(21)-Si(1)-C(17)	114.48(11)
C(1)-N(1)-C(11B)	118.67(19)
C(1)-N(1)-Mn(1)	125.75(15)
C(11B)-N(1)-Mn(1)	115.58(14)
C(4)-O(1)-C(12)	116.11(17)
C(7)-O(2)-Si(1)	121.13(12)
N(1)-C(1)-C(2)	122.2(2)
N(1)-C(1)-H(1)	118.9
C(2)-C(1)-H(1)	118.9
C(3)-C(2)-C(1)	119.5(2)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(3A)	119.8(2)
C(2)-C(3)-H(3)	120.1
C(3A)-C(3)-H(3)	120.1
C(11B)-C(3A)-C(3)	117.1(2)
C(11B)-C(3A)-C(3B)	117.91(18)
C(3)-C(3A)-C(3B)	124.5(2)
C(4)-C(3B)-C(7A)	118.26(19)
C(4)-C(3B)-C(3A)	123.62(19)
C(7A)-C(3B)-C(3A)	118.02(18)
C(4)-C(3B)-Cr(1)	68.93(11)
C(7A)-C(3B)-Cr(1)	67.92(11)
C(3A)-C(3B)-Cr(1)	138.67(14)
O(1)-C(4)-C(5)	116.41(18)
O(1)-C(4)-C(3B)	121.48(19)
C(5)-C(4)-C(3B)	121.96(19)
O(1)-C(4)-Cr(1)	132.22(14)
C(5)-C(4)-Cr(1)	70.42(11)
C(3B)-C(4)-Cr(1)	74.40(11)
C(4)-C(5)-C(6)	119.51(19)
C(4)-C(5)-C(13)	119.05(19)
C(6)-C(5)-C(13)	121.2(2)
C(4)-C(5)-Cr(1)	72.38(11)
C(6)-C(5)-Cr(1)	74.57(12)
C(13)-C(5)-Cr(1)	129.48(14)
C(7)-C(6)-C(5)	118.49(19)
C(7)-C(6)-C(15)	119.04(19)
C(5)-C(6)-C(15)	122.45(19)
C(7)-C(6)-Cr(1)	72.47(12)
C(5)-C(6)-Cr(1)	68.54(11)
C(15)-C(6)-Cr(1)	132.34(14)
O(2)-C(7)-C(6)	117.72(18)
O(2)-C(7)-C(7A)	119.70(18)
C(6)-C(7)-C(7A)	122.57(19)
O(2)-C(7)-Cr(1)	134.89(13)
C(6)-C(7)-Cr(1)	71.68(12)
C(7A)-C(7)-Cr(1)	68.25(11)
C(7)-C(7A)-C(3B)	117.40(18)
C(7)-C(7A)-C(7B)	122.48(18)
C(3B)-C(7A)-C(7B)	120.11(18)
C(7)-C(7A)-Cr(1)	74.70(12)
C(3B)-C(7A)-Cr(1)	74.96(12)
C(7B)-C(7A)-Cr(1)	120.40(13)
C(11A)-C(7B)-C(8)	117.19(19)

C(11A)-C(7B)-C(7A) 118.24(18)
C(8)-C(7B)-C(7A) 124.52(19)
C(9)-C(8)-C(7B) 120.2(2)
C(9)-C(8)-H(8) 119.9
C(7B)-C(8)-H(8) 119.9
C(8)-C(9)-C(10) 121.6(2)
C(8)-C(9)-H(9) 119.2
C(10)-C(9)-H(9) 119.2
C(11)-C(10)-C(9) 121.1(2)
C(11)-C(10)-H(10) 119.5
C(9)-C(10)-H(10) 119.5
C(10)-C(11)-C(11A) 116.25(19)
C(10)-C(11)-Mn(1) 131.23(16)
C(11A)-C(11)-Mn(1) 112.22(14)
C(7B)-C(11A)-C(11) 123.41(19)
C(7B)-C(11A)-C(11B) 120.01(19)
C(11)-C(11A)-C(11B) 116.58(19)
N(1)-C(11B)-C(3A) 122.54(19)
N(1)-C(11B)-C(11A) 114.46(19)
C(3A)-C(11B)-C(11A) 122.97(19)
O(1)-C(12)-H(12A) 109.5(15)
O(1)-C(12)-H(12B) 111.1(15)
H(12A)-C(12)-H(12B) 109(2)
O(1)-C(12)-H(12C) 105.5(15)
H(12A)-C(12)-H(12C) 110(2)
H(12B)-C(12)-H(12C) 111(2)
C(5)-C(13)-C(14) 111.14(18)
C(5)-C(13)-H(13A) 109.4
C(14)-C(13)-H(13A) 109.4
C(5)-C(13)-H(13B) 109.4
C(14)-C(13)-H(13B) 109.4
H(13A)-C(13)-H(13B) 108.0
C(13)-C(14)-H(14A) 109.5
C(13)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14B) 109.5
C(13)-C(14)-H(14C) 109.5
H(14A)-C(14)-H(14C) 109.5
H(14B)-C(14)-H(14C) 109.5
C(13)-C(14)-H(14D) 109.5
H(14A)-C(14)-H(14D) 141.1
H(14B)-C(14)-H(14D) 56.3
H(14C)-C(14)-H(14D) 56.3
C(13)-C(14)-H(14E) 109.5
H(14A)-C(14)-H(14E) 56.3
H(14B)-C(14)-H(14E) 141.1
H(14C)-C(14)-H(14E) 56.3
H(14D)-C(14)-H(14E) 109.5
C(13)-C(14)-H(14F) 109.5
H(14A)-C(14)-H(14F) 56.3
H(14B)-C(14)-H(14F) 56.3
H(14C)-C(14)-H(14F) 141.1
H(14D)-C(14)-H(14F) 109.5
H(14E)-C(14)-H(14F) 109.5
C(6)-C(15)-C(16) 114.06(18)
C(6)-C(15)-H(15A) 108.7
C(16)-C(15)-H(15A) 108.7
C(6)-C(15)-H(15B) 108.7
C(16)-C(15)-H(15B) 108.7
H(15A)-C(15)-H(15B) 107.6
C(15)-C(16)-H(16A) 109.5

C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(16)-H(16D)	109.5
H(16A)-C(16)-H(16D)	141.1
H(16B)-C(16)-H(16D)	56.3
H(16C)-C(16)-H(16D)	56.3
C(15)-C(16)-H(16E)	109.5
H(16A)-C(16)-H(16E)	56.3
H(16B)-C(16)-H(16E)	141.1
H(16C)-C(16)-H(16E)	56.3
H(16D)-C(16)-H(16E)	109.5
C(15)-C(16)-H(16F)	109.5
H(16A)-C(16)-H(16F)	56.3
H(16B)-C(16)-H(16F)	56.3
H(16C)-C(16)-H(16F)	141.1
H(16D)-C(16)-H(16F)	109.5
H(16E)-C(16)-H(16F)	109.5
C(18)-C(17)-C(19)	108.81(19)
C(18)-C(17)-C(20)	109.6(2)
C(19)-C(17)-C(20)	109.0(2)
C(18)-C(17)-Si(1)	112.21(17)
C(19)-C(17)-Si(1)	108.51(16)
C(20)-C(17)-Si(1)	108.66(16)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(18)-H(18D)	109.5
H(18A)-C(18)-H(18D)	141.1
H(18B)-C(18)-H(18D)	56.3
H(18C)-C(18)-H(18D)	56.3
C(17)-C(18)-H(18E)	109.5
H(18A)-C(18)-H(18E)	56.3
H(18B)-C(18)-H(18E)	141.1
H(18C)-C(18)-H(18E)	56.3
H(18D)-C(18)-H(18E)	109.5
C(17)-C(18)-H(18F)	109.5
H(18A)-C(18)-H(18F)	56.3
H(18B)-C(18)-H(18F)	56.3
H(18C)-C(18)-H(18F)	141.1
H(18D)-C(18)-H(18F)	109.5
H(18E)-C(18)-H(18F)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(17)-C(19)-H(19D)	109.5
H(19A)-C(19)-H(19D)	141.1
H(19B)-C(19)-H(19D)	56.3
H(19C)-C(19)-H(19D)	56.3
C(17)-C(19)-H(19E)	109.5
H(19A)-C(19)-H(19E)	56.3
H(19B)-C(19)-H(19E)	141.1

H(19C)-C(19)-H(19E) 56.3
H(19D)-C(19)-H(19E) 109.5
C(17)-C(19)-H(19F) 109.5
H(19A)-C(19)-H(19F) 56.3
H(19B)-C(19)-H(19F) 56.3
H(19C)-C(19)-H(19F) 141.1
H(19D)-C(19)-H(19F) 109.5
H(19E)-C(19)-H(19F) 109.5
C(17)-C(20)-H(20A) 109.5
C(17)-C(20)-H(20B) 109.5
H(20A)-C(20)-H(20B) 109.5
C(17)-C(20)-H(20C) 109.5
H(20A)-C(20)-H(20C) 109.5
H(20B)-C(20)-H(20C) 109.5
C(17)-C(20)-H(20D) 109.5
H(20A)-C(20)-H(20D) 141.1
H(20B)-C(20)-H(20D) 56.3
H(20C)-C(20)-H(20D) 56.3
C(17)-C(20)-H(20E) 109.5
H(20A)-C(20)-H(20E) 56.3
H(20B)-C(20)-H(20E) 141.1
H(20C)-C(20)-H(20E) 56.3
H(20D)-C(20)-H(20E) 109.5
C(17)-C(20)-H(20F) 109.5
H(20A)-C(20)-H(20F) 56.3
H(20B)-C(20)-H(20F) 56.3
H(20C)-C(20)-H(20F) 141.1
H(20D)-C(20)-H(20F) 109.5
H(20E)-C(20)-H(20F) 109.5
Si(1)-C(21)-H(21A) 109.5
Si(1)-C(21)-H(21B) 109.5
H(21A)-C(21)-H(21B) 109.5
Si(1)-C(21)-H(21C) 109.5
H(21A)-C(21)-H(21C) 109.5
H(21B)-C(21)-H(21C) 109.5
Si(1)-C(21)-H(21D) 109.5
H(21A)-C(21)-H(21D) 141.1
H(21B)-C(21)-H(21D) 56.3
H(21C)-C(21)-H(21D) 56.3
Si(1)-C(21)-H(21E) 109.5
H(21A)-C(21)-H(21E) 56.3
H(21B)-C(21)-H(21E) 141.1
H(21C)-C(21)-H(21E) 56.3
H(21D)-C(21)-H(21E) 109.5
Si(1)-C(21)-H(21F) 109.5
H(21A)-C(21)-H(21F) 56.3
H(21B)-C(21)-H(21F) 56.3
H(21C)-C(21)-H(21F) 141.1
H(21D)-C(21)-H(21F) 109.5
H(21E)-C(21)-H(21F) 109.5
Si(1)-C(22)-H(22A) 109.5
Si(1)-C(22)-H(22B) 109.5
H(22A)-C(22)-H(22B) 109.5
Si(1)-C(22)-H(22C) 109.5
H(22A)-C(22)-H(22C) 109.5
H(22B)-C(22)-H(22C) 109.5
Si(1)-C(22)-H(22D) 109.5
H(22A)-C(22)-H(22D) 141.1
H(22B)-C(22)-H(22D) 56.3
H(22C)-C(22)-H(22D) 56.3

Si(1)-C(22)-H(22E)	109.5
H(22A)-C(22)-H(22E)	56.3
H(22B)-C(22)-H(22E)	141.1
H(22C)-C(22)-H(22E)	56.3
H(22D)-C(22)-H(22E)	109.5
Si(1)-C(22)-H(22F)	109.5
H(22A)-C(22)-H(22F)	56.3
H(22B)-C(22)-H(22F)	56.3
H(22C)-C(22)-H(22F)	141.1
H(22D)-C(22)-H(22F)	109.5
H(22E)-C(22)-H(22F)	109.5
O(3)-C(23)-Mn(1)	178.7(2)
O(4)-C(24)-Mn(1)	176.8(2)
O(5)-C(25)-Mn(1)	177.6(2)
O(6)-C(26)-Mn(1)	174.4(2)
O(7)-C(27)-Cr(1)	178.6(2)
O(8)-C(28)-Cr(1)	178.6(2)
O(9)-C(29)-Cr(1)	179.3(2)
Cl(1)-C(30)-Cl(2)	112.67(15)
Cl(1)-C(30)-H(30A)	109.1
Cl(2)-C(30)-H(30A)	109.1
Cl(1)-C(30)-H(30B)	109.1
Cl(2)-C(30)-H(30B)	109.1
H(30A)-C(30)-H(30B)	107.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **34**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mn(1)	18(1)	20(1)	15(1)	3(1)	-1(1)	-3(1)
Cr(1)	14(1)	14(1)	17(1)	0(1)	2(1)	0(1)
Si(1)	18(1)	16(1)	17(1)	0(1)	1(1)	3(1)
N(1)	16(1)	21(1)	17(1)	2(1)	-2(1)	-1(1)
O(1)	21(1)	15(1)	25(1)	-4(1)	1(1)	-5(1)
O(2)	18(1)	13(1)	14(1)	-1(1)	0(1)	2(1)
O(3)	23(1)	40(1)	44(1)	3(1)	9(1)	4(1)
O(4)	36(1)	36(1)	24(1)	-1(1)	-7(1)	7(1)
O(5)	47(1)	34(1)	40(1)	11(1)	-4(1)	-21(1)
O(6)	30(1)	32(1)	29(1)	-7(1)	2(1)	1(1)
O(7)	25(1)	64(1)	30(1)	-19(1)	7(1)	-1(1)
O(8)	21(1)	31(1)	31(1)	-4(1)	-5(1)	-6(1)
O(9)	31(1)	21(1)	48(1)	10(1)	-2(1)	3(1)
C(1)	25(1)	25(1)	17(1)	1(1)	-4(1)	-5(1)
C(2)	29(1)	27(1)	23(1)	-2(1)	-7(1)	-10(1)
C(3)	25(1)	20(1)	24(1)	1(1)	-2(1)	-7(1)
C(3A)	14(1)	18(1)	16(1)	0(1)	0(1)	-2(1)
C(3B)	12(1)	16(1)	18(1)	0(1)	1(1)	-1(1)
C(4)	12(1)	14(1)	22(1)	-1(1)	1(1)	-1(1)
C(5)	12(1)	15(1)	21(1)	2(1)	3(1)	1(1)
C(6)	14(1)	17(1)	18(1)	1(1)	3(1)	4(1)
C(7)	13(1)	14(1)	18(1)	0(1)	1(1)	1(1)

C(7A)	13(1)	14(1)	16(1)	1(1)	0(1)	1(1)
C(7B)	13(1)	13(1)	17(1)	-1(1)	2(1)	1(1)
C(8)	16(1)	16(1)	14(1)	-2(1)	0(1)	-1(1)
C(9)	15(1)	16(1)	20(1)	-3(1)	0(1)	-2(1)
C(10)	16(1)	14(1)	22(1)	4(1)	2(1)	-2(1)
C(11)	15(1)	17(1)	17(1)	1(1)	0(1)	1(1)
C(11A)	11(1)	14(1)	17(1)	0(1)	2(1)	-1(1)
C(11B)	13(1)	19(1)	15(1)	0(1)	1(1)	1(1)
C(12)	31(1)	20(1)	32(2)	-10(1)	4(1)	-3(1)
C(13)	19(1)	16(1)	28(1)	5(1)	3(1)	-2(1)
C(14)	23(1)	30(2)	47(2)	15(1)	8(1)	-4(1)
C(15)	24(1)	18(1)	19(1)	4(1)	5(1)	0(1)
C(16)	31(1)	48(2)	22(1)	6(1)	-3(1)	2(1)
C(17)	24(1)	21(1)	23(1)	-3(1)	0(1)	2(1)
C(18)	42(1)	32(2)	20(1)	1(1)	-4(1)	-14(1)
C(19)	37(1)	23(1)	31(2)	4(1)	-9(1)	-7(1)
C(20)	47(2)	42(2)	37(2)	-21(1)	-5(1)	15(1)
C(21)	19(1)	29(1)	29(1)	-1(1)	1(1)	2(1)
C(22)	30(1)	21(1)	27(1)	3(1)	1(1)	7(1)
C(23)	25(1)	28(1)	18(1)	6(1)	-2(1)	-7(1)
C(24)	22(1)	21(1)	20(1)	0(1)	1(1)	2(1)
C(25)	25(1)	33(2)	20(1)	4(1)	-4(1)	-4(1)
C(26)	24(1)	19(1)	21(1)	5(1)	-4(1)	-8(1)
C(27)	17(1)	27(1)	25(1)	-5(1)	-5(1)	1(1)
C(28)	21(1)	17(1)	16(1)	1(1)	3(1)	4(1)
C(29)	17(1)	22(1)	27(1)	-1(1)	2(1)	-3(1)
C(30)	49(2)	43(2)	29(2)	-1(1)	-6(1)	-1(1)
Cl(1)	52(1)	40(1)	31(1)	-2(1)	-4(1)	5(1)
Cl(2)	95(1)	35(1)	52(1)	-2(1)	-10(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **34**.

	x	y	z	U(eq)
H(1)	8382	7302	5966	27
H(2)	9040	8249	5686	32
H(3)	8747	8564	4872	27
H(8)	5955	6548	3485	18
H(9)	5191	5731	3909	20
H(10)	5593	5520	4732	21
H(12A)	7161(19)	9588(13)	4143(10)	36(8)
H(12B)	7210(19)	9175(12)	4638(10)	30(7)
H(12C)	8020(20)	9752(14)	4569(10)	41(8)
H(13A)	8079	9543	3381	25
H(13B)	7922	9257	2838	25
H(14A)	9610	9546	2839	50
H(14B)	9668	8806	2940	50
H(14C)	9789	9290	3390	50
H(14D)	9768	8882	3273	50
H(14E)	9710	9622	3173	50
H(14F)	9589	9138	2723	50
H(15A)	8054	7687	2396	24
H(15B)	8197	8431	2420	24
H(16A)	6789	8151	1909	50

H(16B)	6421	8579	2362	50
H(16C)	6238	7836	2376	50
H(16D)	6176	8226	2523	50
H(16E)	6544	7798	2069	50
H(16F)	6727	8541	2055	50
H(18A)	7040	6782	1993	47
H(18B)	7386	6252	1607	47
H(18C)	8219	6714	1843	47
H(18D)	8057	6384	1636	47
H(18E)	7711	6913	2022	47
H(18F)	6878	6451	1785	47
H(19A)	6779	5456	2753	46
H(19B)	6583	5386	2171	46
H(19C)	6173	5992	2459	46
H(19D)	6245	5767	2169	46
H(19E)	6441	5837	2752	46
H(19F)	6851	5231	2463	46
H(20A)	8603	5212	2445	63
H(20B)	9222	5742	2151	63
H(20C)	8366	5339	1872	63
H(20D)	8858	5650	1867	63
H(20E)	8238	5120	2161	63
H(20F)	9095	5523	2440	63
H(21A)	9449	7079	2558	38
H(21B)	9979	6525	2866	38
H(21C)	9515	7121	3149	38
H(21D)	9846	6738	3157	38
H(21E)	9316	7292	2849	38
H(21F)	9780	6696	2566	38
H(22A)	7577	5679	3499	39
H(22B)	8454	6101	3745	39
H(22C)	8753	5546	3372	39
H(22D)	8946	5872	3578	39
H(22E)	8069	5450	3332	39
H(22F)	7770	6005	3705	39
H(30A)	11808	5988	4429	48
H(30B)	10769	5833	4717	48

Table 6. Torsion angles [deg] for **34**

C(25)-Mn(1)-N(1)-C(1)	173.8(8)
C(24)-Mn(1)-N(1)-C(1)	-10.68(19)
C(26)-Mn(1)-N(1)-C(1)	-104.67(19)
C(23)-Mn(1)-N(1)-C(1)	86.02(19)
C(11)-Mn(1)-N(1)-C(1)	173.89(19)
C(25)-Mn(1)-N(1)-C(11B)	-7.1(9)
C(24)-Mn(1)-N(1)-C(11B)	168.48(15)
C(26)-Mn(1)-N(1)-C(11B)	74.48(15)
C(23)-Mn(1)-N(1)-C(11B)	-94.82(16)
C(11)-Mn(1)-N(1)-C(11B)	-6.95(14)
C(22)-Si(1)-O(2)-C(7)	80.25(17)
C(21)-Si(1)-O(2)-C(7)	-38.07(17)
C(17)-Si(1)-O(2)-C(7)	-160.12(15)
C(11B)-N(1)-C(1)-C(2)	-1.9(3)
Mn(1)-N(1)-C(1)-C(2)	177.28(17)
N(1)-C(1)-C(2)-C(3)	1.5(4)
C(1)-C(2)-C(3)-C(3A)	1.1(4)

C(2)-C(3)-C(3A)-C(11B)	-3.0(3)
C(2)-C(3)-C(3A)-C(3B)	-175.0(2)
C(11B)-C(3A)-C(3B)-C(4)	177.68(19)
C(3)-C(3A)-C(3B)-C(4)	-10.4(3)
C(11B)-C(3A)-C(3B)-C(7A)	-5.9(3)
C(3)-C(3A)-C(3B)-C(7A)	166.0(2)
C(11B)-C(3A)-C(3B)-Cr(1)	81.8(3)
C(3)-C(3A)-C(3B)-Cr(1)	-106.3(2)
C(27)-Cr(1)-C(3B)-C(4)	-107.65(14)
C(28)-Cr(1)-C(3B)-C(4)	166.83(13)
C(29)-Cr(1)-C(3B)-C(4)	-22.1(2)
C(5)-Cr(1)-C(3B)-C(4)	28.71(12)
C(7A)-Cr(1)-C(3B)-C(4)	134.74(18)
C(6)-Cr(1)-C(3B)-C(4)	65.92(13)
C(7)-Cr(1)-C(3B)-C(4)	101.41(13)
C(27)-Cr(1)-C(3B)-C(7A)	117.61(13)
C(28)-Cr(1)-C(3B)-C(7A)	32.09(16)
C(29)-Cr(1)-C(3B)-C(7A)	-156.87(15)
C(5)-Cr(1)-C(3B)-C(7A)	-106.03(13)
C(4)-Cr(1)-C(3B)-C(7A)	-134.74(18)
C(6)-Cr(1)-C(3B)-C(7A)	-68.81(12)
C(7)-Cr(1)-C(3B)-C(7A)	-33.33(11)
C(27)-Cr(1)-C(3B)-C(3A)	9.8(2)
C(28)-Cr(1)-C(3B)-C(3A)	-75.8(2)
C(29)-Cr(1)-C(3B)-C(3A)	95.3(3)
C(5)-Cr(1)-C(3B)-C(3A)	146.1(2)
C(7A)-Cr(1)-C(3B)-C(3A)	-107.8(3)
C(4)-Cr(1)-C(3B)-C(3A)	117.4(3)
C(6)-Cr(1)-C(3B)-C(3A)	-176.7(2)
C(7)-Cr(1)-C(3B)-C(3A)	-141.2(2)
C(12)-O(1)-C(4)-C(5)	100.5(2)
C(12)-O(1)-C(4)-C(3B)	-83.9(2)
C(12)-O(1)-C(4)-Cr(1)	13.6(3)
C(7A)-C(3B)-C(4)-O(1)	178.68(17)
C(3A)-C(3B)-C(4)-O(1)	-4.9(3)
Cr(1)-C(3B)-C(4)-O(1)	130.32(18)
C(7A)-C(3B)-C(4)-C(5)	-5.9(3)
C(3A)-C(3B)-C(4)-C(5)	170.50(18)
Cr(1)-C(3B)-C(4)-C(5)	-54.25(17)
C(7A)-C(3B)-C(4)-Cr(1)	48.36(16)
C(3A)-C(3B)-C(4)-Cr(1)	-135.26(19)
C(27)-Cr(1)-C(4)-O(1)	-43.2(2)
C(28)-Cr(1)-C(4)-O(1)	-155.7(3)
C(29)-Cr(1)-C(4)-O(1)	47.7(2)
C(5)-Cr(1)-C(4)-O(1)	108.3(2)
C(7A)-Cr(1)-C(4)-O(1)	-146.3(2)
C(6)-Cr(1)-C(4)-O(1)	139.3(2)
C(7)-Cr(1)-C(4)-O(1)	175.7(2)
C(3B)-Cr(1)-C(4)-O(1)	-118.6(2)
C(27)-Cr(1)-C(4)-C(5)	-151.52(14)
C(28)-Cr(1)-C(4)-C(5)	95.9(3)
C(29)-Cr(1)-C(4)-C(5)	-60.65(14)
C(7A)-Cr(1)-C(4)-C(5)	105.36(13)
C(6)-Cr(1)-C(4)-C(5)	30.97(12)
C(7)-Cr(1)-C(4)-C(5)	67.38(12)
C(3B)-Cr(1)-C(4)-C(5)	133.05(18)
C(27)-Cr(1)-C(4)-C(3B)	75.43(14)
C(28)-Cr(1)-C(4)-C(3B)	-37.2(3)
C(29)-Cr(1)-C(4)-C(3B)	166.30(13)
C(5)-Cr(1)-C(4)-C(3B)	-133.05(18)

C(7A)-Cr(1)-C(4)-C(3B)	-27.69(12)
C(6)-Cr(1)-C(4)-C(3B)	-102.08(13)
C(7)-Cr(1)-C(4)-C(3B)	-65.68(12)
O(1)-C(4)-C(5)-C(6)	171.74(17)
C(3B)-C(4)-C(5)-C(6)	-3.9(3)
Cr(1)-C(4)-C(5)-C(6)	-59.97(16)
O(1)-C(4)-C(5)-C(13)	-2.4(3)
C(3B)-C(4)-C(5)-C(13)	-178.02(18)
Cr(1)-C(4)-C(5)-C(13)	125.93(18)
O(1)-C(4)-C(5)-Cr(1)	-128.30(17)
C(3B)-C(4)-C(5)-Cr(1)	56.06(17)
C(27)-Cr(1)-C(5)-C(4)	38.82(18)
C(28)-Cr(1)-C(5)-C(4)	-152.16(15)
C(29)-Cr(1)-C(5)-C(4)	124.09(14)
C(7A)-Cr(1)-C(5)-C(4)	-64.31(13)
C(6)-Cr(1)-C(5)-C(4)	-128.59(18)
C(7)-Cr(1)-C(5)-C(4)	-99.72(13)
C(3B)-Cr(1)-C(5)-C(4)	-28.32(12)
C(27)-Cr(1)-C(5)-C(6)	167.41(14)
C(28)-Cr(1)-C(5)-C(6)	-23.6(2)
C(29)-Cr(1)-C(5)-C(6)	-107.32(14)
C(7A)-Cr(1)-C(5)-C(6)	64.28(13)
C(4)-Cr(1)-C(5)-C(6)	128.59(18)
C(7)-Cr(1)-C(5)-C(6)	28.87(12)
C(3B)-Cr(1)-C(5)-C(6)	100.27(13)
C(27)-Cr(1)-C(5)-C(13)	-74.7(2)
C(28)-Cr(1)-C(5)-C(13)	94.4(2)
C(29)-Cr(1)-C(5)-C(13)	10.6(2)
C(7A)-Cr(1)-C(5)-C(13)	-177.8(2)
C(4)-Cr(1)-C(5)-C(13)	-113.5(2)
C(6)-Cr(1)-C(5)-C(13)	117.9(2)
C(7)-Cr(1)-C(5)-C(13)	146.8(2)
C(3B)-Cr(1)-C(5)-C(13)	-141.8(2)
C(4)-C(5)-C(6)-C(7)	4.4(3)
C(13)-C(5)-C(6)-C(7)	178.41(18)
Cr(1)-C(5)-C(6)-C(7)	-54.44(17)
C(4)-C(5)-C(6)-C(15)	-173.71(18)
C(13)-C(5)-C(6)-C(15)	0.3(3)
Cr(1)-C(5)-C(6)-C(15)	127.42(19)
C(4)-C(5)-C(6)-Cr(1)	58.87(16)
C(13)-C(5)-C(6)-Cr(1)	-127.16(19)
C(27)-Cr(1)-C(6)-C(7)	90.3(4)
C(28)-Cr(1)-C(6)-C(7)	-63.69(14)
C(29)-Cr(1)-C(6)-C(7)	-153.66(13)
C(5)-Cr(1)-C(6)-C(7)	131.43(18)
C(7A)-Cr(1)-C(6)-C(7)	25.92(12)
C(4)-Cr(1)-C(6)-C(7)	100.21(13)
C(3B)-Cr(1)-C(6)-C(7)	63.48(12)
C(27)-Cr(1)-C(6)-C(5)	-41.1(4)
C(28)-Cr(1)-C(6)-C(5)	164.88(13)
C(29)-Cr(1)-C(6)-C(5)	74.91(14)
C(7A)-Cr(1)-C(6)-C(5)	-105.51(13)
C(4)-Cr(1)-C(6)-C(5)	-31.22(12)
C(7)-Cr(1)-C(6)-C(5)	-131.43(18)
C(3B)-Cr(1)-C(6)-C(5)	-67.94(13)
C(27)-Cr(1)-C(6)-C(15)	-156.1(4)
C(28)-Cr(1)-C(6)-C(15)	49.9(2)
C(29)-Cr(1)-C(6)-C(15)	-40.0(2)
C(5)-Cr(1)-C(6)-C(15)	-114.9(3)
C(7A)-Cr(1)-C(6)-C(15)	139.5(2)

C(4)-Cr(1)-C(6)-C(15)	-146.2(2)
C(7)-Cr(1)-C(6)-C(15)	113.6(2)
C(3B)-Cr(1)-C(6)-C(15)	177.1(2)
Si(1)-O(2)-C(7)-C(6)	97.26(19)
Si(1)-O(2)-C(7)-C(7A)	-83.4(2)
Si(1)-O(2)-C(7)-Cr(1)	-171.46(12)
C(5)-C(6)-C(7)-O(2)	-175.70(17)
C(15)-C(6)-C(7)-O(2)	2.5(3)
Cr(1)-C(6)-C(7)-O(2)	131.75(17)
C(5)-C(6)-C(7)-C(7A)	5.0(3)
C(15)-C(6)-C(7)-C(7A)	-176.80(18)
Cr(1)-C(6)-C(7)-C(7A)	-47.56(17)
C(5)-C(6)-C(7)-Cr(1)	52.56(16)
C(15)-C(6)-C(7)-Cr(1)	-129.24(18)
C(27)-Cr(1)-C(7)-O(2)	92.5(2)
C(28)-Cr(1)-C(7)-O(2)	9.4(2)
C(29)-Cr(1)-C(7)-O(2)	-76.3(2)
C(5)-Cr(1)-C(7)-O(2)	-140.9(2)
C(7A)-Cr(1)-C(7)-O(2)	110.8(2)
C(4)-Cr(1)-C(7)-O(2)	-178.7(2)
C(6)-Cr(1)-C(7)-O(2)	-111.2(2)
C(3B)-Cr(1)-C(7)-O(2)	144.2(2)
C(27)-Cr(1)-C(7)-C(6)	-156.33(15)
C(28)-Cr(1)-C(7)-C(6)	120.57(13)
C(29)-Cr(1)-C(7)-C(6)	34.92(17)
C(5)-Cr(1)-C(7)-C(6)	-29.66(12)
C(7A)-Cr(1)-C(7)-C(6)	-137.96(18)
C(4)-Cr(1)-C(7)-C(6)	-67.50(13)
C(3B)-Cr(1)-C(7)-C(6)	-104.57(13)
C(27)-Cr(1)-C(7)-C(7A)	-18.37(19)
C(28)-Cr(1)-C(7)-C(7A)	-101.47(13)
C(29)-Cr(1)-C(7)-C(7A)	172.88(13)
C(5)-Cr(1)-C(7)-C(7A)	108.31(13)
C(4)-Cr(1)-C(7)-C(7A)	70.46(12)
C(6)-Cr(1)-C(7)-C(7A)	137.96(18)
C(3B)-Cr(1)-C(7)-C(7A)	33.39(11)
O(2)-C(7)-C(7A)-C(3B)	166.08(17)
C(6)-C(7)-C(7A)-C(3B)	-14.6(3)
Cr(1)-C(7)-C(7A)-C(3B)	-63.59(16)
O(2)-C(7)-C(7A)-C(7B)	-13.7(3)
C(6)-C(7)-C(7A)-C(7B)	165.57(18)
Cr(1)-C(7)-C(7A)-C(7B)	116.60(18)
O(2)-C(7)-C(7A)-Cr(1)	-130.33(17)
C(6)-C(7)-C(7A)-Cr(1)	48.97(18)
C(4)-C(3B)-C(7A)-C(7)	14.6(3)
C(3A)-C(3B)-C(7A)-C(7)	-161.96(18)
Cr(1)-C(3B)-C(7A)-C(7)	63.45(16)
C(4)-C(3B)-C(7A)-C(7B)	-165.55(18)
C(3A)-C(3B)-C(7A)-C(7B)	17.9(3)
Cr(1)-C(3B)-C(7A)-C(7B)	-116.74(17)
C(4)-C(3B)-C(7A)-Cr(1)	-48.81(16)
C(3A)-C(3B)-C(7A)-Cr(1)	134.60(17)
C(27)-Cr(1)-C(7A)-C(7)	168.31(12)
C(28)-Cr(1)-C(7A)-C(7)	80.01(13)
C(29)-Cr(1)-C(7A)-C(7)	-23.4(4)
C(5)-Cr(1)-C(7A)-C(7)	-61.01(12)
C(4)-Cr(1)-C(7A)-C(7)	-97.21(13)
C(6)-Cr(1)-C(7A)-C(7)	-25.14(11)
C(3B)-Cr(1)-C(7A)-C(7)	-124.58(17)
C(27)-Cr(1)-C(7A)-C(3B)	-67.11(13)

C(28)-Cr(1)-C(7A)-C(3B)	-155.41(12)
C(29)-Cr(1)-C(7A)-C(3B)	101.2(4)
C(5)-Cr(1)-C(7A)-C(3B)	63.57(12)
C(4)-Cr(1)-C(7A)-C(3B)	27.38(11)
C(6)-Cr(1)-C(7A)-C(3B)	99.44(12)
C(7)-Cr(1)-C(7A)-C(3B)	124.58(17)
C(27)-Cr(1)-C(7A)-C(7B)	49.29(18)
C(28)-Cr(1)-C(7A)-C(7B)	-39.01(17)
C(29)-Cr(1)-C(7A)-C(7B)	-142.4(3)
C(5)-Cr(1)-C(7A)-C(7B)	179.97(17)
C(4)-Cr(1)-C(7A)-C(7B)	143.78(18)
C(6)-Cr(1)-C(7A)-C(7B)	-144.16(18)
C(7)-Cr(1)-C(7A)-C(7B)	-119.0(2)
C(3B)-Cr(1)-C(7A)-C(7B)	116.4(2)
C(7)-C(7A)-C(7B)-C(11A)	162.72(19)
C(3B)-C(7A)-C(7B)-C(11A)	-17.1(3)
Cr(1)-C(7A)-C(7B)-C(11A)	-106.65(19)
C(7)-C(7A)-C(7B)-C(8)	-20.1(3)
C(3B)-C(7A)-C(7B)-C(8)	160.1(2)
Cr(1)-C(7A)-C(7B)-C(8)	70.5(2)
C(11A)-C(7B)-C(8)-C(9)	-2.4(3)
C(7A)-C(7B)-C(8)-C(9)	-179.63(19)
C(7B)-C(8)-C(9)-C(10)	-1.8(3)
C(8)-C(9)-C(10)-C(11)	2.4(3)
C(9)-C(10)-C(11)-C(11A)	1.4(3)
C(9)-C(10)-C(11)-Mn(1)	-171.74(16)
C(25)-Mn(1)-C(11)-C(10)	3.1(2)
C(24)-Mn(1)-C(11)-C(10)	138.6(8)
C(26)-Mn(1)-C(11)-C(10)	90.4(2)
C(23)-Mn(1)-C(11)-C(10)	-88.2(2)
N(1)-Mn(1)-C(11)-C(10)	-176.9(2)
C(25)-Mn(1)-C(11)-C(11A)	-170.17(16)
C(24)-Mn(1)-C(11)-C(11A)	-34.7(9)
C(26)-Mn(1)-C(11)-C(11A)	-82.95(16)
C(23)-Mn(1)-C(11)-C(11A)	98.51(16)
N(1)-Mn(1)-C(11)-C(11A)	9.84(14)
C(8)-C(7B)-C(11A)-C(11)	6.4(3)
C(7A)-C(7B)-C(11A)-C(11)	-176.19(18)
C(8)-C(7B)-C(11A)-C(11B)	-173.23(19)
C(7A)-C(7B)-C(11A)-C(11B)	4.2(3)
C(10)-C(11)-C(11A)-C(7B)	-5.9(3)
Mn(1)-C(11)-C(11A)-C(7B)	168.53(16)
C(10)-C(11)-C(11A)-C(11B)	173.79(19)
Mn(1)-C(11)-C(11A)-C(11B)	-11.8(2)
C(1)-N(1)-C(11B)-C(3A)	-0.3(3)
Mn(1)-N(1)-C(11B)-C(3A)	-179.52(15)
C(1)-N(1)-C(11B)-C(11A)	-178.27(19)
Mn(1)-N(1)-C(11B)-C(11A)	2.5(2)
C(3)-C(3A)-C(11B)-N(1)	2.7(3)
C(3B)-C(3A)-C(11B)-N(1)	175.21(18)
C(3)-C(3A)-C(11B)-C(11A)	-179.5(2)
C(3B)-C(3A)-C(11B)-C(11A)	-7.0(3)
C(7B)-C(11A)-C(11B)-N(1)	-174.08(18)
C(11)-C(11A)-C(11B)-N(1)	6.3(3)
C(7B)-C(11A)-C(11B)-C(3A)	8.0(3)
C(11)-C(11A)-C(11B)-C(3A)	-171.70(19)
C(4)-C(5)-C(13)-C(14)	85.7(2)
C(6)-C(5)-C(13)-C(14)	-88.3(3)
Cr(1)-C(5)-C(13)-C(14)	176.25(17)
C(7)-C(6)-C(15)-C(16)	81.0(3)

C(5)-C(6)-C(15)-C(16)	-100.9(2)
Cr(1)-C(6)-C(15)-C(16)	-11.3(3)
O(2)-Si(1)-C(17)-C(18)	55.59(18)
C(22)-Si(1)-C(17)-C(18)	174.81(16)
C(21)-Si(1)-C(17)-C(18)	-62.44(19)
O(2)-Si(1)-C(17)-C(19)	-64.67(17)
C(22)-Si(1)-C(17)-C(19)	54.54(18)
C(21)-Si(1)-C(17)-C(19)	177.29(15)
O(2)-Si(1)-C(17)-C(20)	176.91(17)
C(22)-Si(1)-C(17)-C(20)	-63.9(2)
C(21)-Si(1)-C(17)-C(20)	58.9(2)
C(25)-Mn(1)-C(23)-O(3)	-94(10)
C(24)-Mn(1)-C(23)-O(3)	174(100)
C(26)-Mn(1)-C(23)-O(3)	-9(10)
C(11)-Mn(1)-C(23)-O(3)	-1(10)
N(1)-Mn(1)-C(23)-O(3)	79(10)
C(25)-Mn(1)-C(24)-O(4)	25(4)
C(26)-Mn(1)-C(24)-O(4)	-63(4)
C(23)-Mn(1)-C(24)-O(4)	117(4)
C(11)-Mn(1)-C(24)-O(4)	-110(3)
N(1)-Mn(1)-C(24)-O(4)	-154(4)
C(24)-Mn(1)-C(25)-O(5)	-102(6)
C(26)-Mn(1)-C(25)-O(5)	-8(6)
C(23)-Mn(1)-C(25)-O(5)	161(6)
C(11)-Mn(1)-C(25)-O(5)	73(6)
N(1)-Mn(1)-C(25)-O(5)	73(6)
C(25)-Mn(1)-C(26)-O(6)	43(2)
C(24)-Mn(1)-C(26)-O(6)	134(2)
C(23)-Mn(1)-C(26)-O(6)	-43(2)
C(11)-Mn(1)-C(26)-O(6)	-50(2)
N(1)-Mn(1)-C(26)-O(6)	-130(2)
C(28)-Cr(1)-C(27)-O(7)	-5(10)
C(29)-Cr(1)-C(27)-O(7)	83(10)
C(5)-Cr(1)-C(27)-O(7)	169(100)
C(7A)-Cr(1)-C(27)-O(7)	-100(10)
C(4)-Cr(1)-C(27)-O(7)	-169(100)
C(6)-Cr(1)-C(27)-O(7)	-160(10)
C(7)-Cr(1)-C(27)-O(7)	-88(10)
C(3B)-Cr(1)-C(27)-O(7)	-134(10)
C(27)-Cr(1)-C(28)-O(8)	-11(9)
C(29)-Cr(1)-C(28)-O(8)	-99(9)
C(5)-Cr(1)-C(28)-O(8)	177(100)
C(7A)-Cr(1)-C(28)-O(8)	95(9)
C(4)-Cr(1)-C(28)-O(8)	104(9)
C(6)-Cr(1)-C(28)-O(8)	163(9)
C(7)-Cr(1)-C(28)-O(8)	131(9)
C(3B)-Cr(1)-C(28)-O(8)	76(9)
C(27)-Cr(1)-C(29)-O(9)	-11(24)
C(28)-Cr(1)-C(29)-O(9)	76(24)
C(5)-Cr(1)-C(29)-O(9)	-143(100)
C(7A)-Cr(1)-C(29)-O(9)	-180(100)
C(4)-Cr(1)-C(29)-O(9)	-111(24)
C(6)-Cr(1)-C(29)-O(9)	-178(100)
C(7)-Cr(1)-C(29)-O(9)	162(100)
C(3B)-Cr(1)-C(29)-O(9)	-97(24)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **34** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

2.18 Tetracarbonyl{tricarbonyl(η^6-7b,8,9,10,11,11a-(5,6-diethyl-4-methoxy-7-[(*tert*-butyl)dimethylsilyloxy]dibenzo[*f*,*h*]quinoline-κC^{11}-κN)chromium(0)}manganese(I) (35)

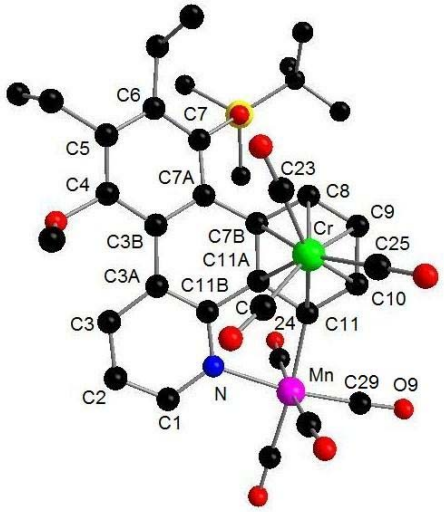


Table 1. Crystal data and structure refinement for **35**.

Empirical formula	C35 H34 Cr Mn N O9 Si
Formula weight	747.66
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 10.5612(3) A alpha = 70.3134(16) deg.
	b = 11.7284(4) A beta = 83.4606(18) deg.
	c = 15.3659(6) A gamma = 77.2105(18) deg.
Volume	1746.00(10) A^3
Z, Calculated density	2, 1.422 Mg/m^3
Absorption coefficient	0.761 mm^-1
F(000)	772
Crystal size	0.80 x 0.60 x 0.60 mm
Theta range for data collection	2.69 to 29.00 deg.

Limiting indices	-14<=h<=14, -15<=k<=15, -17<=l<=20
Reflections collected / unique	21735 / 9256 [R(int) = 0.0426]
Completeness to theta = 29.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.71306 and 0.64194
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9256 / 0 / 441
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1475
R indices (all data)	R1 = 0.0626, wR2 = 0.1551
Largest diff. peak and hole	1.137 and -1.419 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **35**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	467(2)	5174(2)	3443(2)	22(1)
C(2)	-828(3)	5741(2)	3427(2)	23(1)
C(3)	-1178(2)	7008(2)	3174(2)	21(1)
C(3A)	-205(2)	7731(2)	2938(2)	17(1)
C(3B)	-448(2)	9091(2)	2635(2)	17(1)
C(4)	-1673(2)	9834(2)	2717(2)	20(1)
C(5)	-1896(2)	11110(2)	2390(2)	22(1)
C(6)	-891(2)	11706(2)	1886(2)	21(1)
C(7)	321(2)	10984(2)	1776(2)	18(1)
C(7A)	605(2)	9700(2)	2232(2)	16(1)
C(7B)	1946(2)	9012(2)	2391(2)	16(1)
C(8)	3040(2)	9575(2)	2345(2)	19(1)

C(9)	4258(2)	8848(2)	2614(2)	22(1)
C(10)	4448(2)	7539(2)	2925(2)	22(1)
C(11)	3422(2)	6929(2)	2971(2)	19(1)
C(11A)	2176(2)	7703(2)	2746(2)	17(1)
C(11B)	1079(2)	7079(2)	2947(2)	17(1)
C(12)	-2689(3)	8966(3)	4162(2)	38(1)
C(13)	-3223(3)	11854(3)	2532(2)	29(1)
C(14)	-4068(3)	12166(4)	1710(3)	44(1)
C(15)	-1030(3)	13093(2)	1551(2)	26(1)
C(16)	-441(3)	13496(3)	2238(2)	35(1)
C(17)	1944(3)	10183(3)	-53(2)	32(1)
C(18)	30(3)	12623(3)	-543(2)	30(1)
C(19)	2906(3)	12587(3)	-264(2)	28(1)
C(20)	4206(3)	11708(3)	25(2)	39(1)
C(21)	2975(3)	13131(4)	-1325(2)	44(1)
C(22)	2705(4)	13621(3)	163(3)	48(1)
C(23)	1819(3)	9723(3)	4043(2)	30(1)
C(24)	1780(3)	7438(3)	4681(2)	29(1)
C(25)	3888(3)	8146(3)	4723(2)	31(1)
C(26)	3446(3)	5556(2)	1901(2)	27(1)
C(27)	3437(2)	4776(2)	4466(2)	23(1)
C(28)	3230(3)	3523(3)	3326(2)	28(1)
C(29)	5157(3)	4708(2)	3179(2)	23(1)
Cr	2814(1)	8355(1)	3780(1)	21(1)
Mn	3400(1)	5106(1)	3195(1)	19(1)
N	1424(2)	5830(2)	3200(2)	19(1)
O(1)	-2708(2)	9282(2)	3177(1)	25(1)
O(2)	1275(2)	11569(2)	1235(1)	19(1)
O(3)	1164(3)	10575(2)	4180(2)	45(1)
O(4)	1105(2)	6956(2)	5198(2)	37(1)

O(5)	4576(2)	7994(2)	5283(2)	41(1)
O(7)	3535(2)	4546(2)	5232(2)	34(1)
O(6)	3509(3)	5842(2)	1121(2)	43(1)
O(8)	3149(2)	2544(2)	3388(2)	41(1)
O(9)	6269(2)	4492(2)	3174(2)	30(1)
Si	1524(1)	11730(1)	105(1)	19(1)

Table 3. Bond lengths [A] and angles [deg] for **35**.

C(1)-N	1.348(3)
C(1)-C(2)	1.381(4)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.377(4)
C(2)-H(2A)	0.9500
C(3)-C(3A)	1.414(3)
C(3)-H(3A)	0.9500
C(3A)-C(11B)	1.401(3)
C(3A)-C(3B)	1.475(3)
C(3B)-C(4)	1.409(3)
C(3B)-C(7A)	1.424(3)
C(4)-C(5)	1.383(4)
C(4)-O(1)	1.393(3)
C(5)-C(6)	1.411(4)
C(5)-C(13)	1.513(3)
C(6)-C(7)	1.398(3)
C(6)-C(15)	1.510(3)
C(7)-O(2)	1.381(3)
C(7)-C(7A)	1.409(3)
C(7A)-C(7B)	1.469(3)

C(7B)-C(11A)	1.419(3)
C(7B)-C(8)	1.436(3)
C(7B)-Cr	2.239(2)
C(8)-C(9)	1.397(3)
C(8)-Cr	2.207(2)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.420(3)
C(9)-Cr	2.224(3)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.408(3)
C(10)-Cr	2.285(3)
C(10)-H(10A)	0.9500
C(11)-C(11A)	1.428(3)
C(11)-Mn	2.053(2)
C(11)-Cr	2.345(3)
C(11A)-C(11B)	1.454(3)
C(11A)-Cr	2.203(2)
C(11B)-N	1.357(3)
C(12)-O(1)	1.433(4)
C(12)-H(12C)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12A)	0.9800
C(13)-C(14)	1.526(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14C)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14A)	0.9800
C(15)-C(16)	1.531(4)
C(15)-H(15A)	0.9900

C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-Si	1.860(3)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-Si	1.871(3)
C(18)-H(18C)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18A)	0.9800
C(19)-C(22)	1.529(5)
C(19)-C(20)	1.533(4)
C(19)-C(21)	1.537(4)
C(19)-Si	1.882(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(3)	1.151(4)
C(23)-Cr	1.853(3)
C(24)-O(4)	1.099(4)
C(24)-Cr	1.853(3)
C(25)-O(5)	1.132(4)

C(25)-Cr	1.860(3)
C(26)-O(6)	1.129(4)
C(26)-Mn	1.874(3)
C(27)-O(7)	1.127(3)
C(27)-Mn	1.862(3)
C(28)-O(8)	1.142(3)
C(28)-Mn	1.846(3)
C(29)-O(9)	1.145(3)
C(29)-Mn	1.809(3)
Mn-N	2.072(2)
O(2)-Si	1.6774(19)
N-C(1)-C(2)	121.8(2)
N-C(1)-H(1A)	119.1
C(2)-C(1)-H(1A)	119.1
C(3)-C(2)-C(1)	120.3(2)
C(3)-C(2)-H(2A)	119.8
C(1)-C(2)-H(2A)	119.8
C(2)-C(3)-C(3A)	119.8(2)
C(2)-C(3)-H(3A)	120.1
C(3A)-C(3)-H(3A)	120.1
C(11B)-C(3A)-C(3)	115.9(2)
C(11B)-C(3A)-C(3B)	118.8(2)
C(3)-C(3A)-C(3B)	125.2(2)
C(4)-C(3B)-C(7A)	117.6(2)
C(4)-C(3B)-C(3A)	123.7(2)
C(7A)-C(3B)-C(3A)	118.7(2)
C(5)-C(4)-O(1)	117.3(2)
C(5)-C(4)-C(3B)	122.9(2)
O(1)-C(4)-C(3B)	119.8(2)
C(4)-C(5)-C(6)	119.2(2)

C(4)-C(5)-C(13) 120.2(2)

C(6)-C(5)-C(13) 120.5(2)

C(7)-C(6)-C(5) 118.6(2)

C(7)-C(6)-C(15) 118.5(2)

C(5)-C(6)-C(15) 122.5(2)

O(2)-C(7)-C(6) 118.2(2)

O(2)-C(7)-C(7A) 119.9(2)

C(6)-C(7)-C(7A) 121.9(2)

C(7)-C(7A)-C(3B) 118.2(2)

C(7)-C(7A)-C(7B) 121.9(2)

C(3B)-C(7A)-C(7B) 119.5(2)

C(11A)-C(7B)-C(8) 116.2(2)

C(11A)-C(7B)-C(7A) 119.1(2)

C(8)-C(7B)-C(7A) 124.0(2)

C(11A)-C(7B)-Cr 70.01(14)

C(8)-C(7B)-Cr 69.94(14)

C(7A)-C(7B)-Cr 122.37(16)

C(9)-C(8)-C(7B) 120.6(2)

C(9)-C(8)-Cr 72.28(14)

C(7B)-C(8)-Cr 72.37(13)

C(9)-C(8)-H(8A) 119.7

C(7B)-C(8)-H(8A) 119.7

Cr-C(8)-H(8A) 127.8

C(8)-C(9)-C(10) 120.9(2)

C(8)-C(9)-Cr 70.98(14)

C(10)-C(9)-Cr 74.01(14)

C(8)-C(9)-H(9A) 119.5

C(10)-C(9)-H(9A) 119.5

Cr-C(9)-H(9A) 127.6

C(11)-C(10)-C(9) 121.4(2)

C(11)-C(10)-Cr 74.62(15)

C(9)-C(10)-Cr 69.31(15)

C(11)-C(10)-H(10A) 119.3

C(9)-C(10)-H(10A) 119.3

Cr-C(10)-H(10A) 129.2

C(10)-C(11)-C(11A) 116.0(2)

C(10)-C(11)-Mn 131.59(18)

C(11A)-C(11)-Mn 112.20(16)

C(10)-C(11)-Cr 69.99(15)

C(11A)-C(11)-Cr 66.38(13)

Mn-C(11)-Cr 137.84(12)

C(7B)-C(11A)-C(11) 124.6(2)

C(7B)-C(11A)-C(11B) 119.2(2)

C(11)-C(11A)-C(11B) 116.0(2)

C(7B)-C(11A)-Cr 72.76(14)

C(11)-C(11A)-Cr 77.18(14)

C(11B)-C(11A)-Cr 121.02(17)

N-C(11B)-C(3A) 124.3(2)

N-C(11B)-C(11A) 113.9(2)

C(3A)-C(11B)-C(11A) 121.6(2)

O(1)-C(12)-H(12C) 109.5

O(1)-C(12)-H(12B) 109.5

H(12C)-C(12)-H(12B) 109.5

O(1)-C(12)-H(12A) 109.5

H(12C)-C(12)-H(12A) 109.5

H(12B)-C(12)-H(12A) 109.5

C(5)-C(13)-C(14) 111.5(2)

C(5)-C(13)-H(13A) 109.3

C(14)-C(13)-H(13A) 109.3

C(5)-C(13)-H(13B) 109.3

C(14)-C(13)-H(13B) 109.3

H(13A)-C(13)-H(13B) 108.0

C(13)-C(14)-H(14C) 109.5

C(13)-C(14)-H(14B) 109.5

H(14C)-C(14)-H(14B) 109.5

C(13)-C(14)-H(14A) 109.5

H(14C)-C(14)-H(14A) 109.5

H(14B)-C(14)-H(14A) 109.5

C(6)-C(15)-C(16) 109.8(2)

C(6)-C(15)-H(15A) 109.7

C(16)-C(15)-H(15A) 109.7

C(6)-C(15)-H(15B) 109.7

C(16)-C(15)-H(15B) 109.7

H(15A)-C(15)-H(15B) 108.2

C(15)-C(16)-H(16A) 109.5

C(15)-C(16)-H(16B) 109.5

H(16A)-C(16)-H(16B) 109.5

C(15)-C(16)-H(16C) 109.5

H(16A)-C(16)-H(16C) 109.5

H(16B)-C(16)-H(16C) 109.5

Si-C(17)-H(17A) 109.5

Si-C(17)-H(17B) 109.5

H(17A)-C(17)-H(17B) 109.5

Si-C(17)-H(17C) 109.5

H(17A)-C(17)-H(17C) 109.5

H(17B)-C(17)-H(17C) 109.5

Si-C(18)-H(18C) 109.5

Si-C(18)-H(18B) 109.5

H(18C)-C(18)-H(18B) 109.5

Si-C(18)-H(18A) 109.5

H(18C)-C(18)-H(18A)	109.5
H(18B)-C(18)-H(18A)	109.5
C(22)-C(19)-C(20)	109.6(3)
C(22)-C(19)-C(21)	109.9(3)
C(20)-C(19)-C(21)	107.2(3)
C(22)-C(19)-Si	110.2(2)
C(20)-C(19)-Si	110.73(19)
C(21)-C(19)-Si	109.1(2)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(3)-C(23)-Cr	177.1(3)
O(4)-C(24)-Cr	175.6(3)
O(5)-C(25)-Cr	177.5(3)
O(6)-C(26)-Mn	177.8(3)

O(7)-C(27)-Mn	175.9(2)
O(8)-C(28)-Mn	178.2(3)
O(9)-C(29)-Mn	177.7(2)
C(23)-Cr-C(24)	86.16(13)
C(23)-Cr-C(25)	88.54(14)
C(24)-Cr-C(25)	87.02(13)
C(23)-Cr-C(11A)	119.72(11)
C(24)-Cr-C(11A)	89.83(11)
C(25)-Cr-C(11A)	151.30(11)
C(23)-Cr-C(8)	87.41(12)
C(24)-Cr-C(8)	148.16(11)
C(25)-Cr-C(8)	123.96(11)
C(11A)-Cr-C(8)	66.69(9)
C(23)-Cr-C(9)	112.81(11)
C(24)-Cr-C(9)	160.64(11)
C(25)-Cr-C(9)	96.89(12)
C(11A)-Cr-C(9)	77.63(9)
C(8)-Cr-C(9)	36.75(9)
C(23)-Cr-C(7B)	90.03(11)
C(24)-Cr-C(7B)	111.14(11)
C(25)-Cr-C(7B)	161.65(11)
C(11A)-Cr-C(7B)	37.23(8)
C(8)-Cr-C(7B)	37.69(8)
C(9)-Cr-C(7B)	66.92(9)
C(23)-Cr-C(10)	149.47(11)
C(24)-Cr-C(10)	124.34(11)
C(25)-Cr-C(10)	93.89(12)
C(11A)-Cr-C(10)	64.77(9)
C(8)-Cr-C(10)	66.09(9)
C(9)-Cr-C(10)	36.68(9)

C(7B)-Cr-C(10)	78.30(9)
C(23)-Cr-C(11)	155.80(11)
C(24)-Cr-C(11)	95.91(11)
C(25)-Cr-C(11)	115.62(12)
C(11A)-Cr-C(11)	36.44(8)
C(8)-Cr-C(11)	78.13(9)
C(9)-Cr-C(11)	65.28(9)
C(7B)-Cr-C(11)	66.68(8)
C(10)-Cr-C(11)	35.39(8)
C(29)-Mn-C(28)	93.24(12)
C(29)-Mn-C(27)	87.43(12)
C(28)-Mn-C(27)	93.04(12)
C(29)-Mn-C(26)	90.15(12)
C(28)-Mn-C(26)	91.82(13)
C(27)-Mn-C(26)	174.69(11)
C(29)-Mn-C(11)	91.66(10)
C(28)-Mn-C(11)	174.14(11)
C(27)-Mn-C(11)	90.39(10)
C(26)-Mn-C(11)	84.96(11)
C(29)-Mn-N	171.19(10)
C(28)-Mn-N	95.56(10)
C(27)-Mn-N	91.69(10)
C(26)-Mn-N	89.98(10)
C(11)-Mn-N	79.57(9)
C(1)-N-C(11B)	117.9(2)
C(1)-N-Mn	125.94(17)
C(11B)-N-Mn	116.17(15)
C(4)-O(1)-C(12)	112.7(2)
C(7)-O(2)-Si	122.41(15)
O(2)-Si-C(17)	109.83(12)

O(2)-Si-C(18)	110.79(11)
C(17)-Si-C(18)	108.54(14)
O(2)-Si-C(19)	103.72(11)
C(17)-Si-C(19)	112.31(14)
C(18)-Si-C(19)	111.61(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **35**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	26(1)	19(1)	22(1)	-4(1)	1(1)	-11(1)
C(2)	24(1)	25(1)	24(1)	-7(1)	2(1)	-13(1)
C(3)	18(1)	26(1)	20(1)	-7(1)	1(1)	-8(1)
C(3A)	20(1)	20(1)	12(1)	-3(1)	0(1)	-7(1)
C(3B)	19(1)	19(1)	13(1)	-5(1)	-2(1)	-5(1)
C(4)	18(1)	27(1)	16(1)	-9(1)	-1(1)	-6(1)
C(5)	23(1)	25(1)	19(1)	-11(1)	-3(1)	1(1)
C(6)	27(1)	20(1)	16(1)	-7(1)	-6(1)	-2(1)
C(7)	24(1)	17(1)	13(1)	-4(1)	-2(1)	-6(1)
C(7A)	19(1)	17(1)	12(1)	-4(1)	-1(1)	-4(1)
C(7B)	19(1)	16(1)	12(1)	-2(1)	0(1)	-5(1)
C(8)	22(1)	19(1)	15(1)	1(1)	-2(1)	-9(1)
C(9)	20(1)	23(1)	20(1)	1(1)	-1(1)	-10(1)
C(10)	18(1)	21(1)	21(1)	1(1)	-2(1)	-4(1)
C(11)	19(1)	17(1)	17(1)	0(1)	-1(1)	-4(1)
C(11A)	18(1)	16(1)	14(1)	-1(1)	-1(1)	-5(1)

C(11B)	20(1)	18(1)	13(1)	-2(1)	-1(1)	-7(1)
C(12)	38(2)	49(2)	24(2)	-11(1)	9(1)	-12(1)
C(13)	25(1)	31(1)	31(2)	-14(1)	-1(1)	3(1)
C(14)	28(2)	53(2)	46(2)	-18(2)	-13(1)	9(1)
C(15)	33(1)	17(1)	26(1)	-7(1)	-7(1)	3(1)
C(16)	49(2)	24(1)	35(2)	-14(1)	-7(1)	-5(1)
C(17)	39(2)	30(1)	29(2)	-14(1)	2(1)	-8(1)
C(18)	31(1)	37(2)	18(1)	-6(1)	-5(1)	-4(1)
C(19)	30(1)	27(1)	22(1)	2(1)	-2(1)	-12(1)
C(20)	29(1)	44(2)	36(2)	2(1)	-7(1)	-14(1)
C(21)	39(2)	57(2)	24(2)	9(1)	0(1)	-16(2)
C(22)	61(2)	35(2)	54(2)	-13(2)	8(2)	-31(2)
C(23)	34(1)	28(1)	26(2)	-8(1)	-5(1)	-5(1)
C(24)	37(2)	23(1)	28(2)	-6(1)	-7(1)	-6(1)
C(25)	32(1)	24(1)	33(2)	3(1)	-16(1)	-8(1)
C(26)	28(1)	25(1)	28(2)	-8(1)	0(1)	-5(1)
C(27)	20(1)	18(1)	27(1)	-4(1)	0(1)	-1(1)
C(28)	29(1)	24(1)	30(2)	-7(1)	-1(1)	-4(1)
C(29)	31(1)	16(1)	19(1)	-3(1)	1(1)	-4(1)
Cr	22(1)	20(1)	20(1)	-3(1)	-2(1)	-5(1)
Mn	21(1)	16(1)	18(1)	-2(1)	0(1)	-3(1)
N	22(1)	17(1)	17(1)	-3(1)	-1(1)	-7(1)
O(1)	18(1)	33(1)	25(1)	-11(1)	3(1)	-7(1)
O(2)	25(1)	15(1)	14(1)	0(1)	-2(1)	-6(1)
O(3)	52(1)	36(1)	46(2)	-20(1)	-6(1)	5(1)
O(4)	35(1)	52(1)	27(1)	-14(1)	10(1)	-15(1)
O(5)	37(1)	56(2)	30(1)	-10(1)	-4(1)	-12(1)
O(7)	34(1)	38(1)	22(1)	-7(1)	-1(1)	1(1)
O(6)	56(2)	51(1)	23(1)	-11(1)	1(1)	-14(1)
O(8)	46(1)	23(1)	57(2)	-12(1)	-2(1)	-10(1)

O(9)	24(1)	26(1)	36(1)	-8(1)	1(1)	-1(1)
Si	24(1)	19(1)	15(1)	-3(1)	-2(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **35**.

	x	y	z	U(eq)
H(1A)	690	4299	3630	27
H(2A)	-1480	5254	3591	28
H(3A)	-2070	7395	3158	25
H(8A)	2934	10449	2131	23
H(9A)	4969	9234	2587	27
H(10A)	5285	7065	3107	26
H(12C)	-3437	8590	4451	57
H(12B)	-2731	9714	4324	57
H(12A)	-1884	8379	4383	57
H(13A)	-3121	12628	2618	35
H(13B)	-3658	11376	3100	35
H(14C)	-4926	12629	1830	66
H(14B)	-4166	11401	1622	66
H(14A)	-3657	12668	1152	66
H(15A)	-1961	13488	1487	32
H(15B)	-581	13361	936	32
H(16A)	479	13103	2300	52
H(16B)	-902	13248	2842	52
H(16C)	-524	14396	2013	52
H(17A)	2140	10281	-710	47
H(17B)	1208	9762	166	47

H(17C)	2706	9692	303	47
H(18C)	-76	13497	-602	44
H(18B)	-731	12305	-207	44
H(18A)	116	12535	-1161	44
H(20A)	4894	12187	-87	58
H(20B)	4410	11139	-337	58
H(20C)	4146	11236	685	58
H(21A)	3057	12469	-1594	67
H(21B)	3730	13529	-1524	67
H(21C)	2181	13743	-1533	67
H(22A)	3427	14065	-39	72
H(22B)	2674	13266	839	72
H(22C)	1886	14195	-38	72

Table 6. Torsion angles [deg] for **35**.

N-C(1)-C(2)-C(3)	-1.2(4)
C(1)-C(2)-C(3)-C(3A)	-0.6(4)
C(2)-C(3)-C(3A)-C(11B)	2.5(4)
C(2)-C(3)-C(3A)-C(3B)	178.5(2)
C(11B)-C(3A)-C(3B)-C(4)	-171.0(2)
C(3)-C(3A)-C(3B)-C(4)	13.1(4)
C(11B)-C(3A)-C(3B)-C(7A)	9.3(3)
C(3)-C(3A)-C(3B)-C(7A)	-166.6(2)
C(7A)-C(3B)-C(4)-C(5)	2.8(4)
C(3A)-C(3B)-C(4)-C(5)	-176.9(2)
C(7A)-C(3B)-C(4)-O(1)	-174.5(2)
C(3A)-C(3B)-C(4)-O(1)	5.7(4)
O(1)-C(4)-C(5)-C(6)	-177.4(2)

C(3B)-C(4)-C(5)-C(6)	5.2(4)
O(1)-C(4)-C(5)-C(13)	-0.3(4)
C(3B)-C(4)-C(5)-C(13)	-177.7(2)
C(4)-C(5)-C(6)-C(7)	-3.3(4)
C(13)-C(5)-C(6)-C(7)	179.7(2)
C(4)-C(5)-C(6)-C(15)	-176.6(2)
C(13)-C(5)-C(6)-C(15)	6.3(4)
C(5)-C(6)-C(7)-O(2)	176.1(2)
C(15)-C(6)-C(7)-O(2)	-10.3(3)
C(5)-C(6)-C(7)-C(7A)	-6.9(4)
C(15)-C(6)-C(7)-C(7A)	166.7(2)
O(2)-C(7)-C(7A)-C(3B)	-168.1(2)
C(6)-C(7)-C(7A)-C(3B)	14.9(4)
O(2)-C(7)-C(7A)-C(7B)	18.8(3)
C(6)-C(7)-C(7A)-C(7B)	-158.2(2)
C(4)-C(3B)-C(7A)-C(7)	-12.5(3)
C(3A)-C(3B)-C(7A)-C(7)	167.2(2)
C(4)-C(3B)-C(7A)-C(7B)	160.7(2)
C(3A)-C(3B)-C(7A)-C(7B)	-19.5(3)
C(7)-C(7A)-C(7B)-C(11A)	-171.9(2)
C(3B)-C(7A)-C(7B)-C(11A)	15.1(3)
C(7)-C(7A)-C(7B)-C(8)	18.0(4)
C(3B)-C(7A)-C(7B)-C(8)	-155.0(2)
C(7)-C(7A)-C(7B)-Cr	104.4(2)
C(3B)-C(7A)-C(7B)-Cr	-68.5(3)
C(11A)-C(7B)-C(8)-C(9)	1.9(4)
C(7A)-C(7B)-C(8)-C(9)	172.2(2)
Cr-C(7B)-C(8)-C(9)	56.0(2)
C(11A)-C(7B)-C(8)-Cr	-54.15(19)
C(7A)-C(7B)-C(8)-Cr	116.2(2)

C(7B)-C(8)-C(9)-C(10)	0.8(4)
Cr-C(8)-C(9)-C(10)	56.9(2)
C(7B)-C(8)-C(9)-Cr	-56.1(2)
C(8)-C(9)-C(10)-C(11)	0.3(4)
Cr-C(9)-C(10)-C(11)	55.8(2)
C(8)-C(9)-C(10)-Cr	-55.5(2)
C(9)-C(10)-C(11)-C(11A)	-4.0(4)
Cr-C(10)-C(11)-C(11A)	49.4(2)
C(9)-C(10)-C(11)-Mn	169.6(2)
Cr-C(10)-C(11)-Mn	-137.0(2)
C(9)-C(10)-C(11)-Cr	-53.4(2)
C(8)-C(7B)-C(11A)-C(11)	-6.1(4)
C(7A)-C(7B)-C(11A)-C(11)	-176.9(2)
Cr-C(7B)-C(11A)-C(11)	-60.2(2)
C(8)-C(7B)-C(11A)-C(11B)	170.5(2)
C(7A)-C(7B)-C(11A)-C(11B)	-0.3(3)
Cr-C(7B)-C(11A)-C(11B)	116.4(2)
C(8)-C(7B)-C(11A)-Cr	54.11(19)
C(7A)-C(7B)-C(11A)-Cr	-116.7(2)
C(10)-C(11)-C(11A)-C(7B)	7.1(4)
Mn-C(11)-C(11A)-C(7B)	-167.72(19)
Cr-C(11)-C(11A)-C(7B)	58.2(2)
C(10)-C(11)-C(11A)-C(11B)	-169.6(2)
Mn-C(11)-C(11A)-C(11B)	15.6(3)
Cr-C(11)-C(11A)-C(11B)	-118.5(2)
C(10)-C(11)-C(11A)-Cr	-51.1(2)
Mn-C(11)-C(11A)-Cr	134.06(14)
C(3)-C(3A)-C(11B)-N	-2.8(4)
C(3B)-C(3A)-C(11B)-N	-179.1(2)
C(3)-C(3A)-C(11B)-C(11A)	-178.1(2)

C(3B)-C(3A)-C(11B)-C(11A)	5.6(4)
C(7B)-C(11A)-C(11B)-N	174.2(2)
C(11)-C(11A)-C(11B)-N	-8.9(3)
Cr-C(11A)-C(11B)-N	-99.3(2)
C(7B)-C(11A)-C(11B)-C(3A)	-10.1(4)
C(11)-C(11A)-C(11B)-C(3A)	166.8(2)
Cr-C(11A)-C(11B)-C(3A)	76.5(3)
C(4)-C(5)-C(13)-C(14)	-92.6(3)
C(6)-C(5)-C(13)-C(14)	84.5(3)
C(7)-C(6)-C(15)-C(16)	-77.1(3)
C(5)-C(6)-C(15)-C(16)	96.2(3)
O(3)-C(23)-Cr-C(24)	-86(6)
O(3)-C(23)-Cr-C(25)	-173(6)
O(3)-C(23)-Cr-C(11A)	1(6)
O(3)-C(23)-Cr-C(8)	62(6)
O(3)-C(23)-Cr-C(9)	90(6)
O(3)-C(23)-Cr-C(7B)	25(6)
O(3)-C(23)-Cr-C(10)	91(6)
O(3)-C(23)-Cr-C(11)	10(6)
O(4)-C(24)-Cr-C(23)	33(4)
O(4)-C(24)-Cr-C(25)	122(4)
O(4)-C(24)-Cr-C(11A)	-86(4)
O(4)-C(24)-Cr-C(8)	-45(4)
O(4)-C(24)-Cr-C(9)	-135(3)
O(4)-C(24)-Cr-C(7B)	-55(4)
O(4)-C(24)-Cr-C(10)	-145(3)
O(4)-C(24)-Cr-C(11)	-122(4)
O(5)-C(25)-Cr-C(23)	-159(6)
O(5)-C(25)-Cr-C(24)	114(6)
O(5)-C(25)-Cr-C(11A)	30(6)

O(5)-C(25)-Cr-C(8)	-74(6)
O(5)-C(25)-Cr-C(9)	-47(6)
O(5)-C(25)-Cr-C(7B)	-74(6)
O(5)-C(25)-Cr-C(10)	-10(6)
O(5)-C(25)-Cr-C(11)	19(6)
C(7B)-C(11A)-Cr-C(23)	41.39(18)
C(11)-C(11A)-Cr-C(23)	174.31(15)
C(11B)-C(11A)-Cr-C(23)	-72.8(2)
C(7B)-C(11A)-Cr-C(24)	126.87(15)
C(11)-C(11A)-Cr-C(24)	-100.21(15)
C(11B)-C(11A)-Cr-C(24)	12.7(2)
C(7B)-C(11A)-Cr-C(25)	-149.7(2)
C(11)-C(11A)-Cr-C(25)	-16.7(3)
C(11B)-C(11A)-Cr-C(25)	96.1(3)
C(7B)-C(11A)-Cr-C(8)	-31.00(13)
C(11)-C(11A)-Cr-C(8)	101.92(15)
C(11B)-C(11A)-Cr-C(8)	-145.2(2)
C(7B)-C(11A)-Cr-C(9)	-67.99(14)
C(11)-C(11A)-Cr-C(9)	64.93(14)
C(11B)-C(11A)-Cr-C(9)	177.8(2)
C(11)-C(11A)-Cr-C(7B)	132.92(19)
C(11B)-C(11A)-Cr-C(7B)	-114.2(2)
C(7B)-C(11A)-Cr-C(10)	-104.45(15)
C(11)-C(11A)-Cr-C(10)	28.47(13)
C(11B)-C(11A)-Cr-C(10)	141.3(2)
C(7B)-C(11A)-Cr-C(11)	-132.92(19)
C(11B)-C(11A)-Cr-C(11)	112.9(2)
C(9)-C(8)-Cr-C(23)	135.17(17)
C(7B)-C(8)-Cr-C(23)	-93.41(16)
C(9)-C(8)-Cr-C(24)	-146.4(2)

C(7B)-C(8)-Cr-C(24)	-14.9(3)
C(9)-C(8)-Cr-C(25)	48.7(2)
C(7B)-C(8)-Cr-C(25)	-179.90(16)
C(9)-C(8)-Cr-C(11A)	-100.78(16)
C(7B)-C(8)-Cr-C(11A)	30.64(13)
C(7B)-C(8)-Cr-C(9)	131.4(2)
C(9)-C(8)-Cr-C(7B)	-131.4(2)
C(9)-C(8)-Cr-C(10)	-29.25(15)
C(7B)-C(8)-Cr-C(10)	102.18(15)
C(9)-C(8)-Cr-C(11)	-64.35(15)
C(7B)-C(8)-Cr-C(11)	67.07(14)
C(8)-C(9)-Cr-C(23)	-49.82(18)
C(10)-C(9)-Cr-C(23)	178.57(16)
C(8)-C(9)-Cr-C(24)	118.2(3)
C(10)-C(9)-Cr-C(24)	-13.4(4)
C(8)-C(9)-Cr-C(25)	-141.14(16)
C(10)-C(9)-Cr-C(25)	87.26(17)
C(8)-C(9)-Cr-C(11A)	67.46(15)
C(10)-C(9)-Cr-C(11A)	-64.15(15)
C(10)-C(9)-Cr-C(8)	-131.6(2)
C(8)-C(9)-Cr-C(7B)	29.89(14)
C(10)-C(9)-Cr-C(7B)	-101.72(16)
C(8)-C(9)-Cr-C(10)	131.6(2)
C(8)-C(9)-Cr-C(11)	103.78(16)
C(10)-C(9)-Cr-C(11)	-27.83(14)
C(11A)-C(7B)-Cr-C(23)	-144.96(15)
C(8)-C(7B)-Cr-C(23)	85.72(16)
C(7A)-C(7B)-Cr-C(23)	-32.55(19)
C(11A)-C(7B)-Cr-C(24)	-59.06(16)
C(8)-C(7B)-Cr-C(24)	171.62(16)

C(7A)-C(7B)-Cr-C(24)	53.3(2)
C(11A)-C(7B)-Cr-C(25)	129.6(4)
C(8)-C(7B)-Cr-C(25)	0.3(4)
C(7A)-C(7B)-Cr-C(25)	-118.0(4)
C(8)-C(7B)-Cr-C(11A)	-129.3(2)
C(7A)-C(7B)-Cr-C(11A)	112.4(2)
C(11A)-C(7B)-Cr-C(8)	129.3(2)
C(7A)-C(7B)-Cr-C(8)	-118.3(2)
C(11A)-C(7B)-Cr-C(9)	100.13(15)
C(8)-C(7B)-Cr-C(9)	-29.19(14)
C(7A)-C(7B)-Cr-C(9)	-147.5(2)
C(11A)-C(7B)-Cr-C(10)	63.45(14)
C(8)-C(7B)-Cr-C(10)	-65.87(14)
C(7A)-C(7B)-Cr-C(10)	175.86(19)
C(11A)-C(7B)-Cr-C(11)	28.27(13)
C(8)-C(7B)-Cr-C(11)	-101.05(15)
C(7A)-C(7B)-Cr-C(11)	140.7(2)
C(11)-C(10)-Cr-C(23)	-135.5(2)
C(9)-C(10)-Cr-C(23)	-2.6(3)
C(11)-C(10)-Cr-C(24)	41.7(2)
C(9)-C(10)-Cr-C(24)	174.64(17)
C(11)-C(10)-Cr-C(25)	130.76(16)
C(9)-C(10)-Cr-C(25)	-96.32(17)
C(11)-C(10)-Cr-C(11A)	-29.27(14)
C(9)-C(10)-Cr-C(11A)	103.66(16)
C(11)-C(10)-Cr-C(8)	-103.63(16)
C(9)-C(10)-Cr-C(8)	29.30(15)
C(11)-C(10)-Cr-C(9)	-132.9(2)
C(11)-C(10)-Cr-C(7B)	-66.02(15)
C(9)-C(10)-Cr-C(7B)	66.91(15)

C(9)-C(10)-Cr-C(11)	132.9(2)
C(10)-C(11)-Cr-C(23)	119.7(3)
C(11A)-C(11)-Cr-C(23)	-12.1(3)
Mn-C(11)-Cr-C(23)	-109.7(3)
C(10)-C(11)-Cr-C(24)	-146.46(16)
C(11A)-C(11)-Cr-C(24)	81.66(16)
Mn-C(11)-Cr-C(24)	-15.9(2)
C(10)-C(11)-Cr-C(25)	-56.94(18)
C(11A)-C(11)-Cr-C(25)	171.18(15)
Mn-C(11)-Cr-C(25)	73.6(2)
C(10)-C(11)-Cr-C(11A)	131.9(2)
Mn-C(11)-Cr-C(11A)	-97.6(2)
C(10)-C(11)-Cr-C(8)	65.21(15)
C(11A)-C(11)-Cr-C(8)	-66.67(14)
Mn-C(11)-Cr-C(8)	-164.22(19)
C(10)-C(11)-Cr-C(9)	28.79(15)
C(11A)-C(11)-Cr-C(9)	-103.09(15)
Mn-C(11)-Cr-C(9)	159.4(2)
C(10)-C(11)-Cr-C(7B)	103.03(16)
C(11A)-C(11)-Cr-C(7B)	-28.85(13)
Mn-C(11)-Cr-C(7B)	-126.40(19)
C(11A)-C(11)-Cr-C(10)	-131.9(2)
Mn-C(11)-Cr-C(10)	130.6(3)
O(9)-C(29)-Mn-C(28)	-166(6)
O(9)-C(29)-Mn-C(27)	-73(6)
O(9)-C(29)-Mn-C(26)	102(6)
O(9)-C(29)-Mn-C(11)	17(6)
O(9)-C(29)-Mn-N	11(7)
O(8)-C(28)-Mn-C(29)	-46(9)
O(8)-C(28)-Mn-C(27)	-134(9)

O(8)-C(28)-Mn-C(26)	44(9)
O(8)-C(28)-Mn-C(11)	100(9)
O(8)-C(28)-Mn-N	134(9)
O(7)-C(27)-Mn-C(29)	-11(3)
O(7)-C(27)-Mn-C(28)	82(3)
O(7)-C(27)-Mn-C(26)	-74(4)
O(7)-C(27)-Mn-C(11)	-103(3)
O(7)-C(27)-Mn-N	177(100)
O(6)-C(26)-Mn-C(29)	-37(7)
O(6)-C(26)-Mn-C(28)	-130(7)
O(6)-C(26)-Mn-C(27)	26(8)
O(6)-C(26)-Mn-C(11)	55(7)
O(6)-C(26)-Mn-N	135(7)
C(10)-C(11)-Mn-C(29)	-5.4(3)
C(11A)-C(11)-Mn-C(29)	168.37(19)
Cr-C(11)-Mn-C(29)	-112.81(18)
C(10)-C(11)-Mn-C(28)	-152.2(10)
C(11A)-C(11)-Mn-C(28)	21.6(12)
Cr-C(11)-Mn-C(28)	100.4(11)
C(10)-C(11)-Mn-C(27)	82.0(3)
C(11A)-C(11)-Mn-C(27)	-104.19(19)
Cr-C(11)-Mn-C(27)	-25.37(18)
C(10)-C(11)-Mn-C(26)	-95.4(3)
C(11A)-C(11)-Mn-C(26)	78.37(19)
Cr-C(11)-Mn-C(26)	157.19(19)
C(10)-C(11)-Mn-N	173.7(3)
C(11A)-C(11)-Mn-N	-12.54(17)
Cr-C(11)-Mn-N	66.27(17)
C(2)-C(1)-N-C(11B)	0.9(4)
C(2)-C(1)-N-Mn	179.8(2)

C(3A)-C(11B)-N-C(1)	1.2(4)
C(11A)-C(11B)-N-C(1)	176.8(2)
C(3A)-C(11B)-N-Mn	-177.84(19)
C(11A)-C(11B)-N-Mn	-2.2(3)
C(29)-Mn-N-C(1)	-164.6(6)
C(28)-Mn-N-C(1)	12.7(2)
C(27)-Mn-N-C(1)	-80.6(2)
C(26)-Mn-N-C(1)	104.5(2)
C(11)-Mn-N-C(1)	-170.6(2)
C(29)-Mn-N-C(11B)	14.3(8)
C(28)-Mn-N-C(11B)	-168.37(19)
C(27)-Mn-N-C(11B)	98.41(19)
C(26)-Mn-N-C(11B)	-76.55(19)
C(11)-Mn-N-C(11B)	8.33(18)
C(5)-C(4)-O(1)-C(12)	-95.6(3)
C(3B)-C(4)-O(1)-C(12)	81.9(3)
C(6)-C(7)-O(2)-Si	-93.5(2)
C(7A)-C(7)-O(2)-Si	89.3(2)
C(7)-O(2)-Si-C(17)	-60.1(2)
C(7)-O(2)-Si-C(18)	59.8(2)
C(7)-O(2)-Si-C(19)	179.68(18)
C(22)-C(19)-Si-O(2)	-42.6(3)
C(20)-C(19)-Si-O(2)	78.9(2)
C(21)-C(19)-Si-O(2)	-163.4(2)
C(22)-C(19)-Si-C(17)	-161.2(2)
C(20)-C(19)-Si-C(17)	-39.7(3)
C(21)-C(19)-Si-C(17)	78.1(3)
C(22)-C(19)-Si-C(18)	76.7(3)
C(20)-C(19)-Si-C(18)	-161.8(2)
C(21)-C(19)-Si-C(18)	-44.1(3)

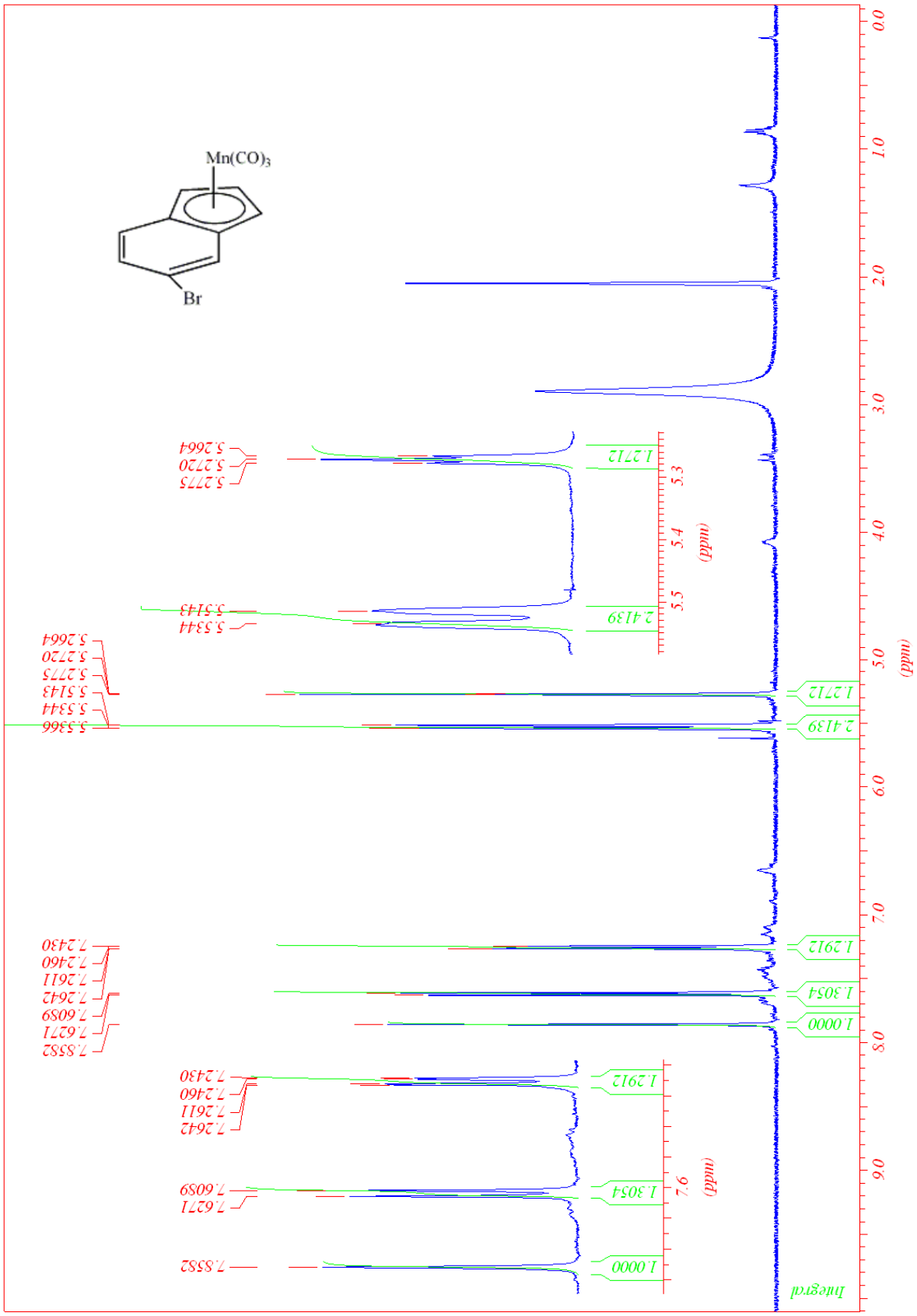
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **35** [A and deg.].

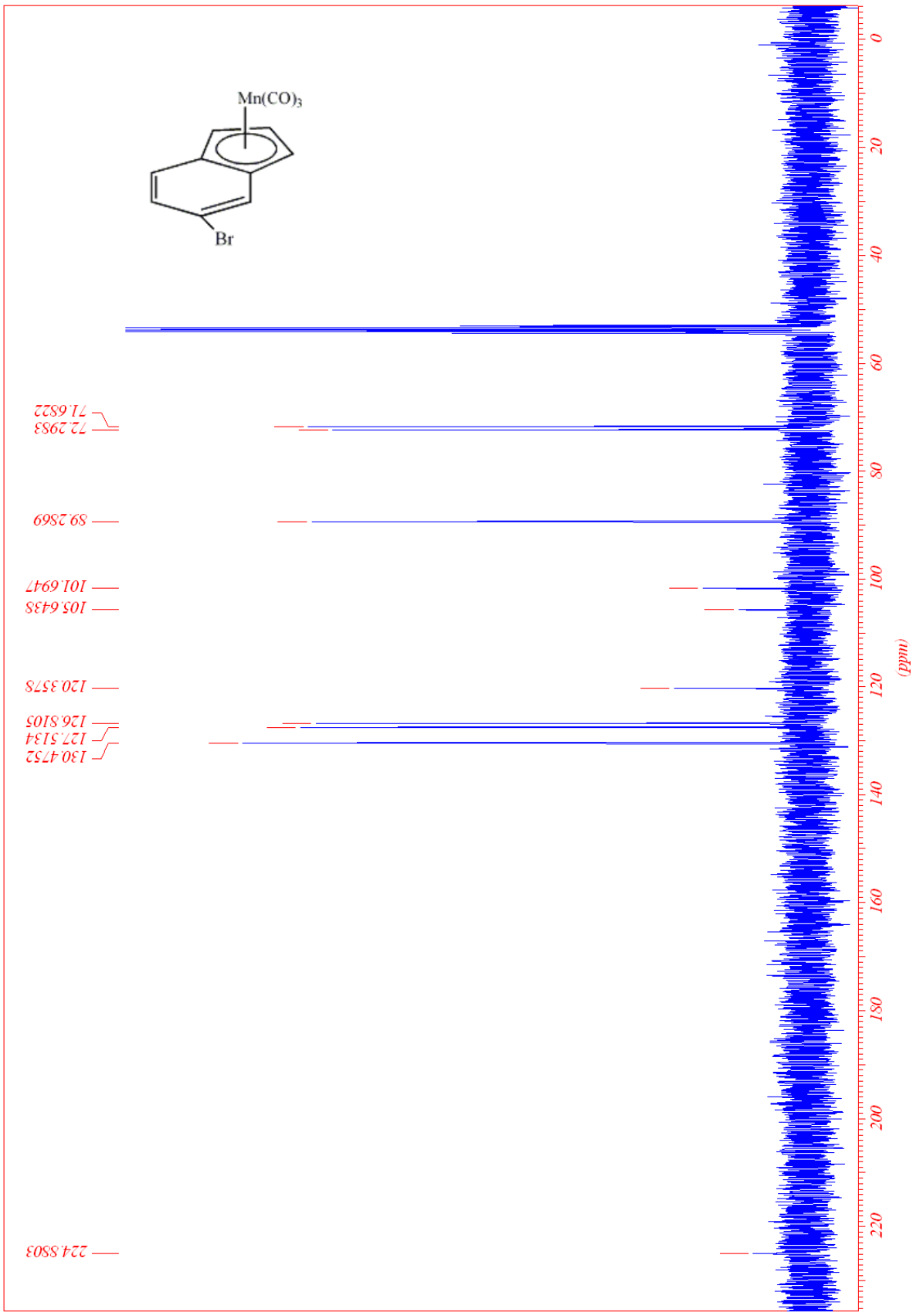
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

3. ^{1}H-NMR and ^{13}C-NMR spectra of organometallic compounds

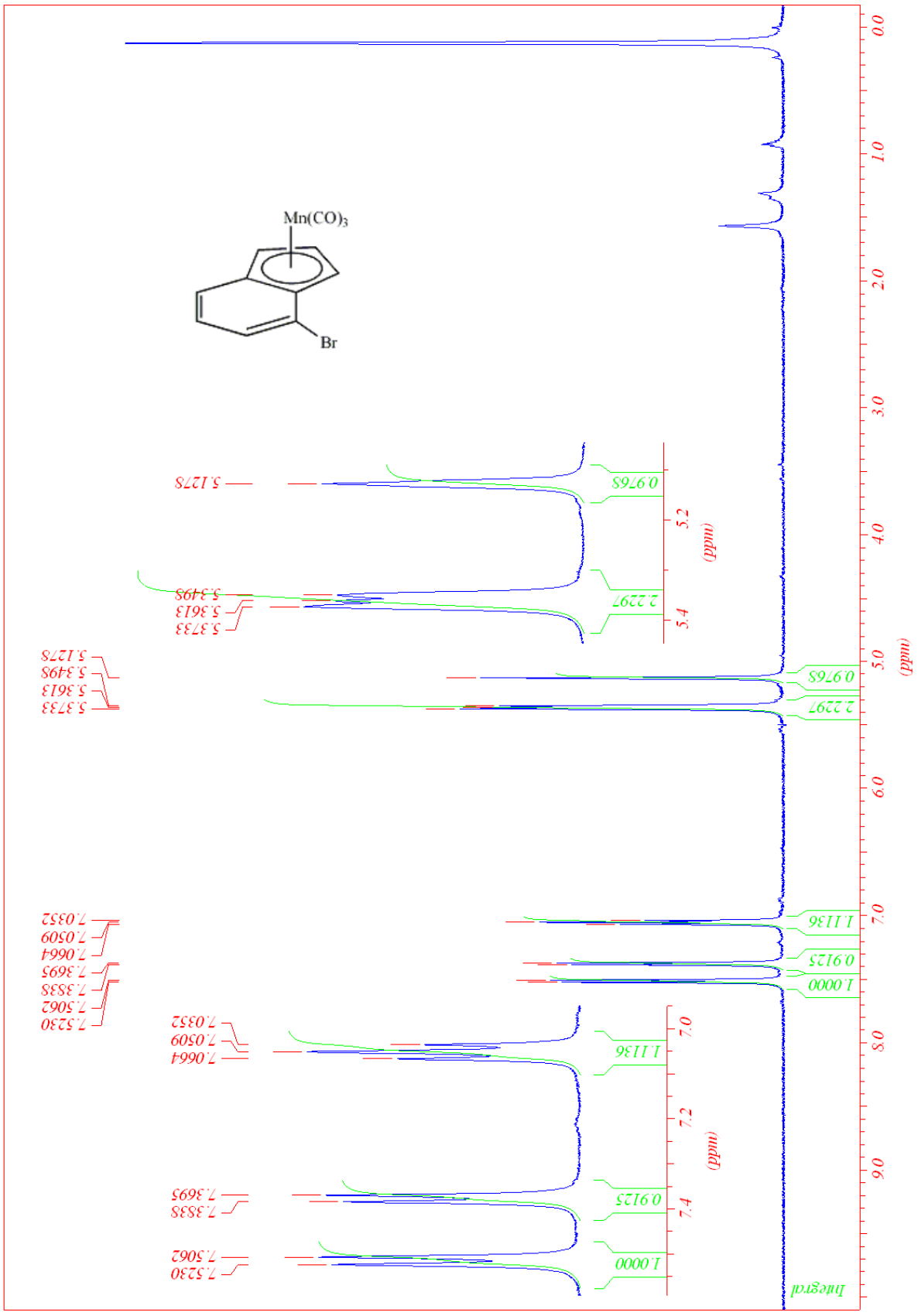
^{1}H-NMR Spectrum of complex 3



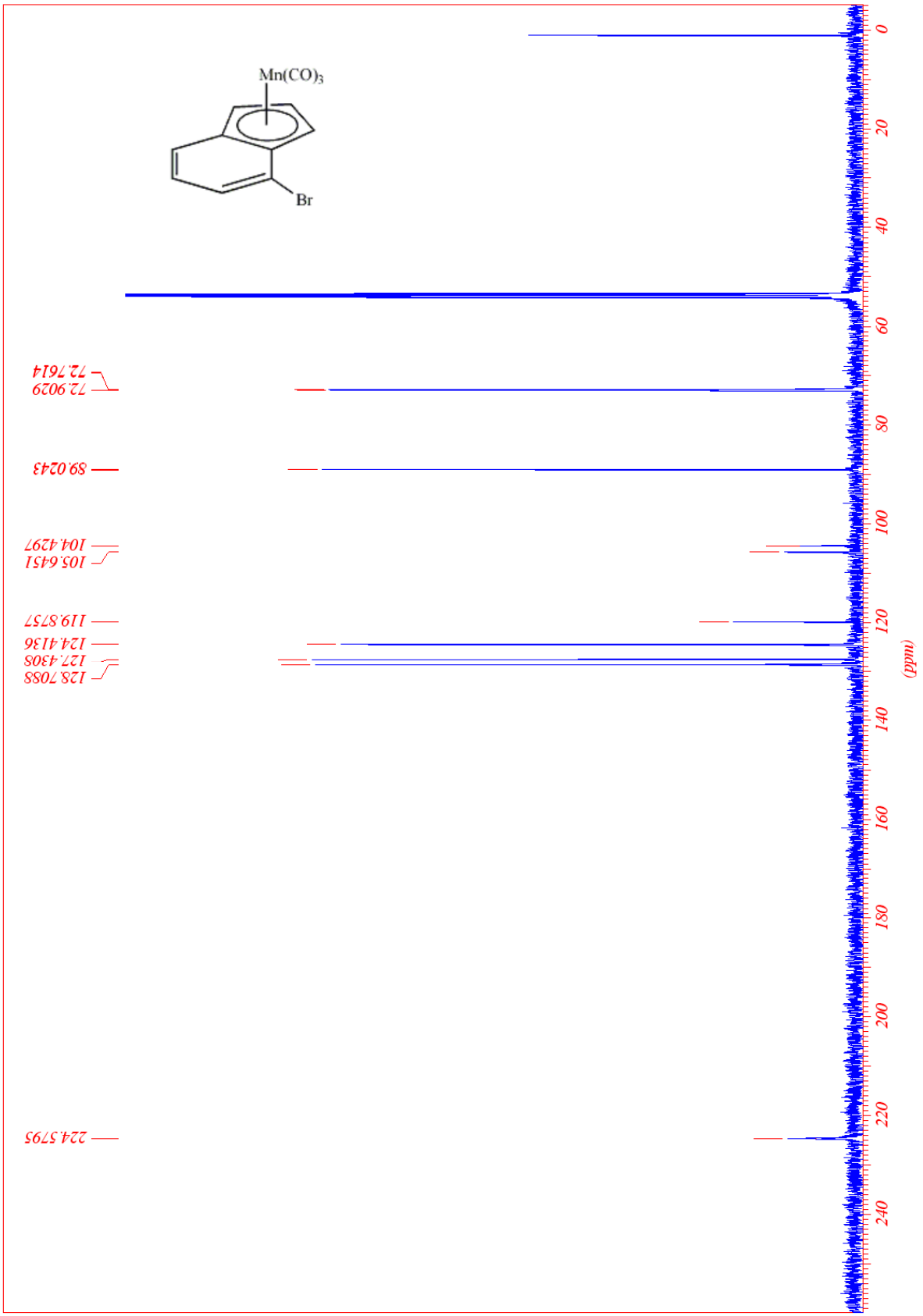
^{13}C-NMR spectrum of complex 3



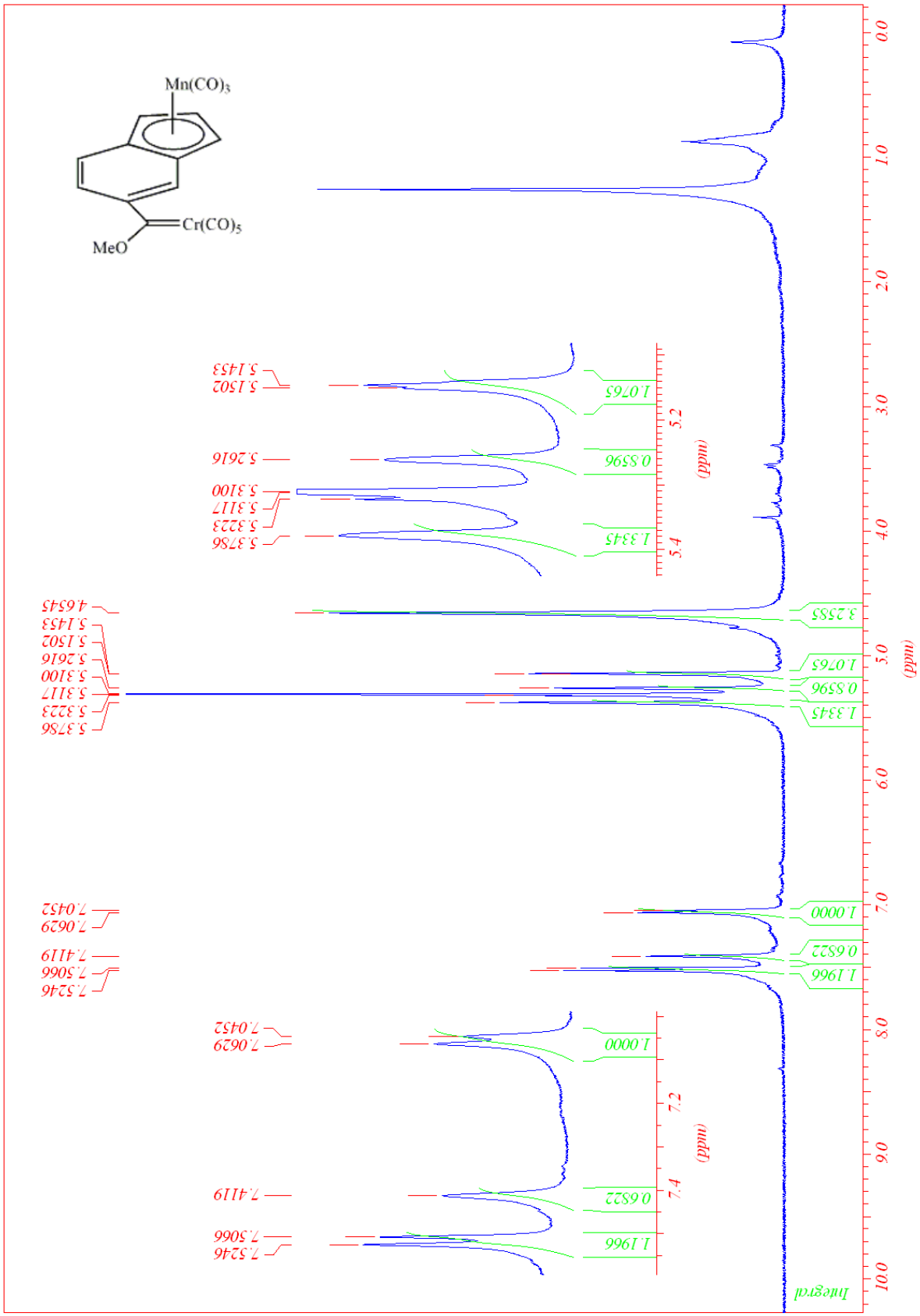
[1]H-NMR Spectrum of complex 4



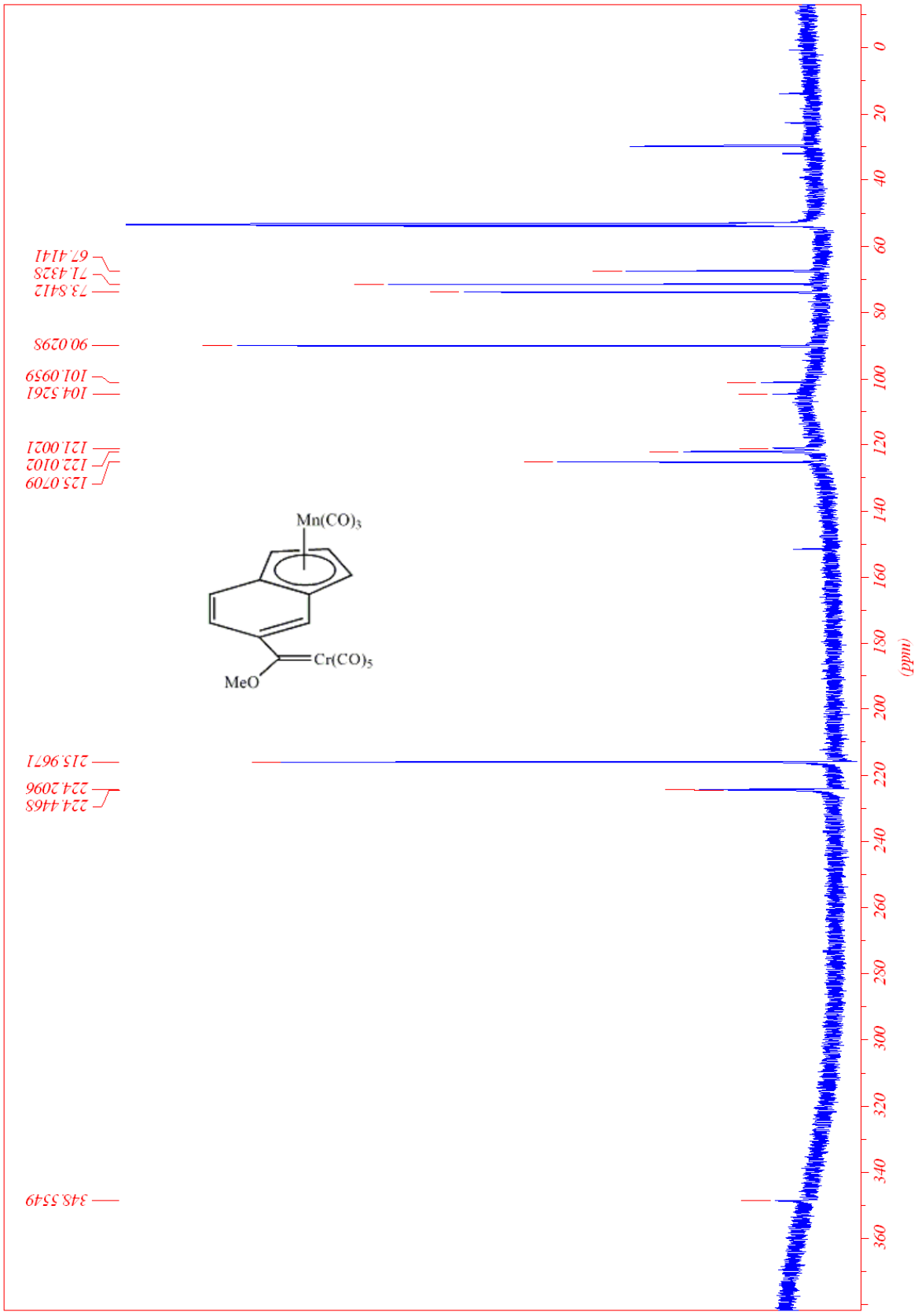
^{13}C-NMR spectrum of complex 4



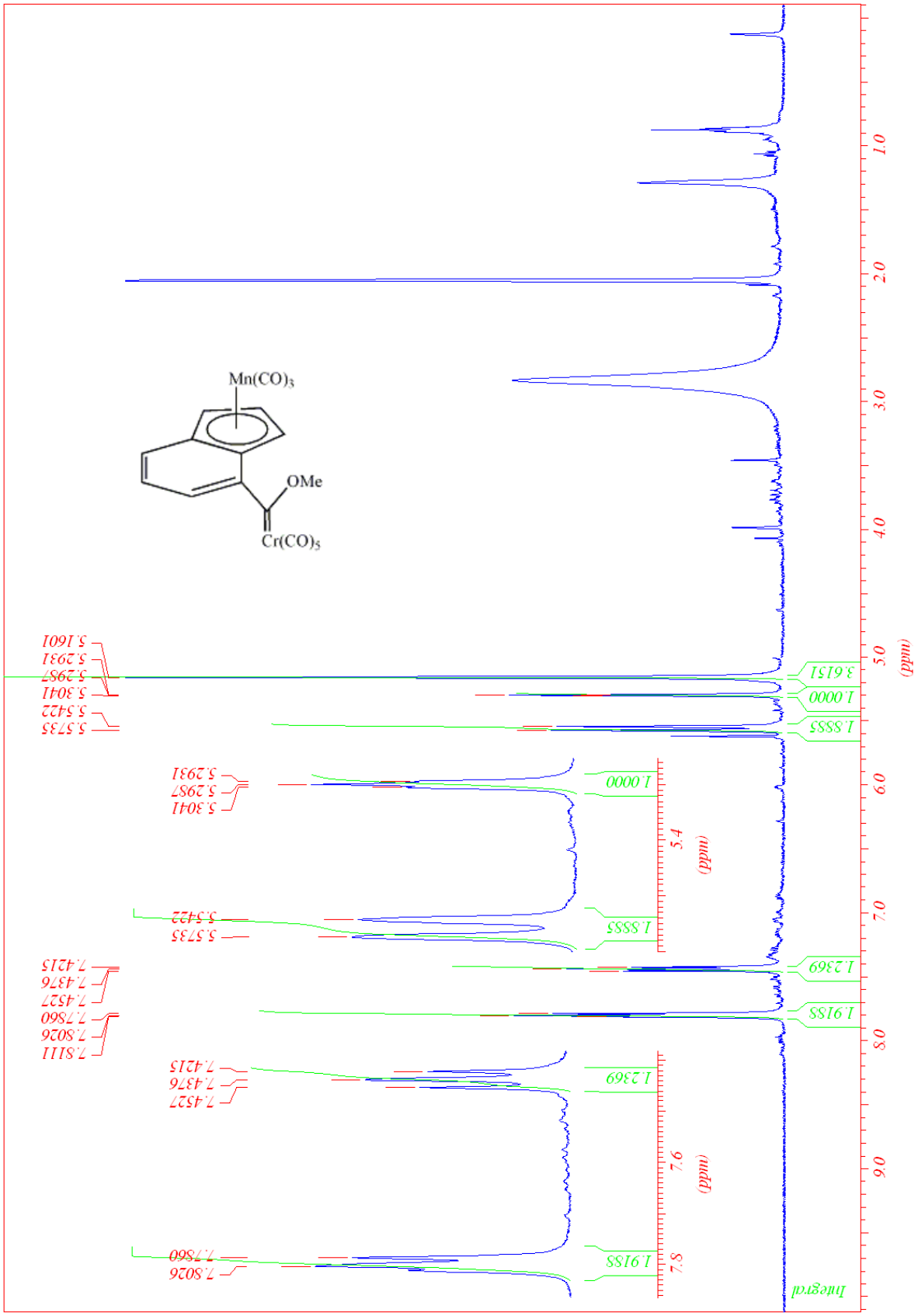
[1]H-NMR Spectrum of complex 5



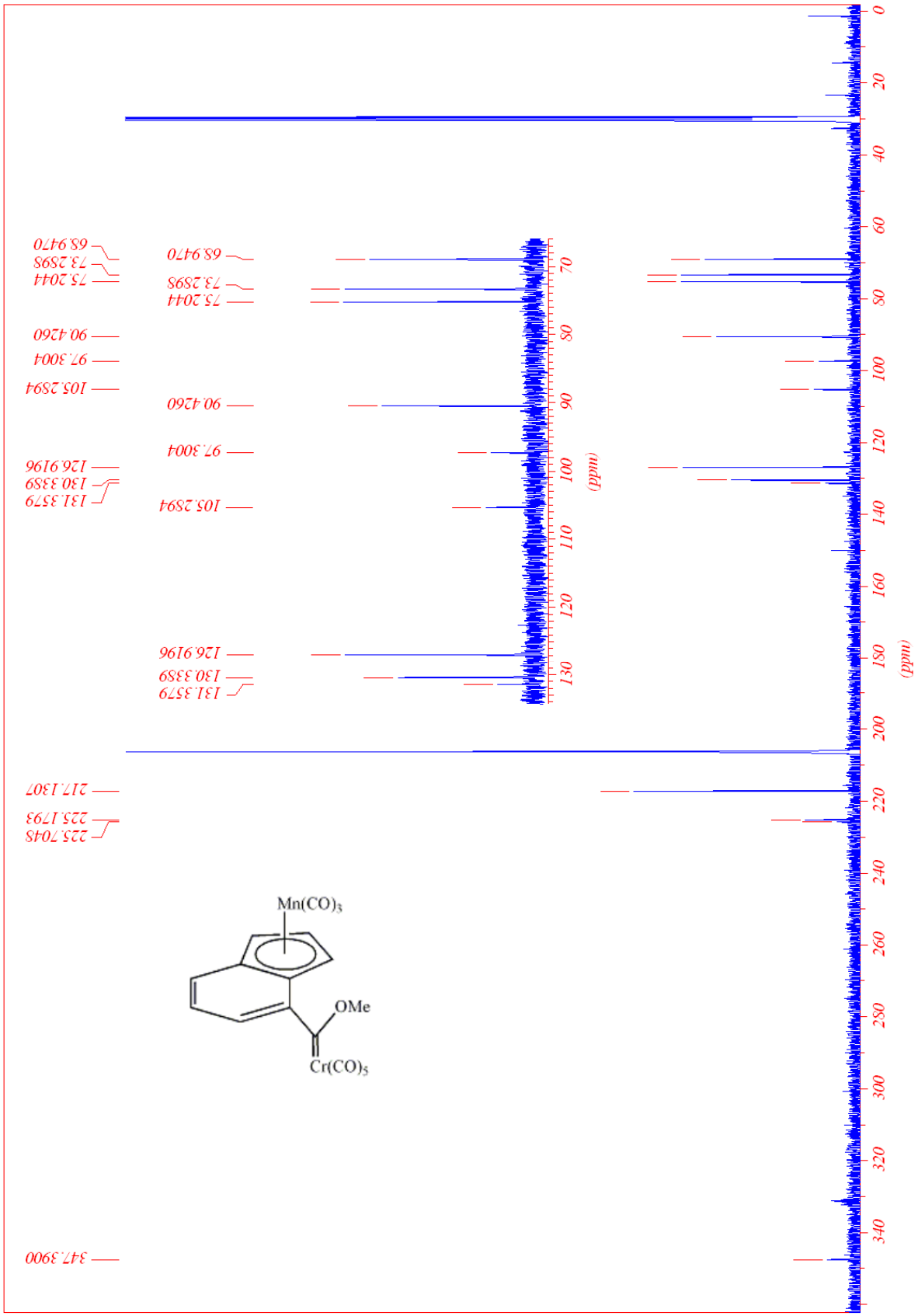
^{13}C-NMR spectrum of complex 5



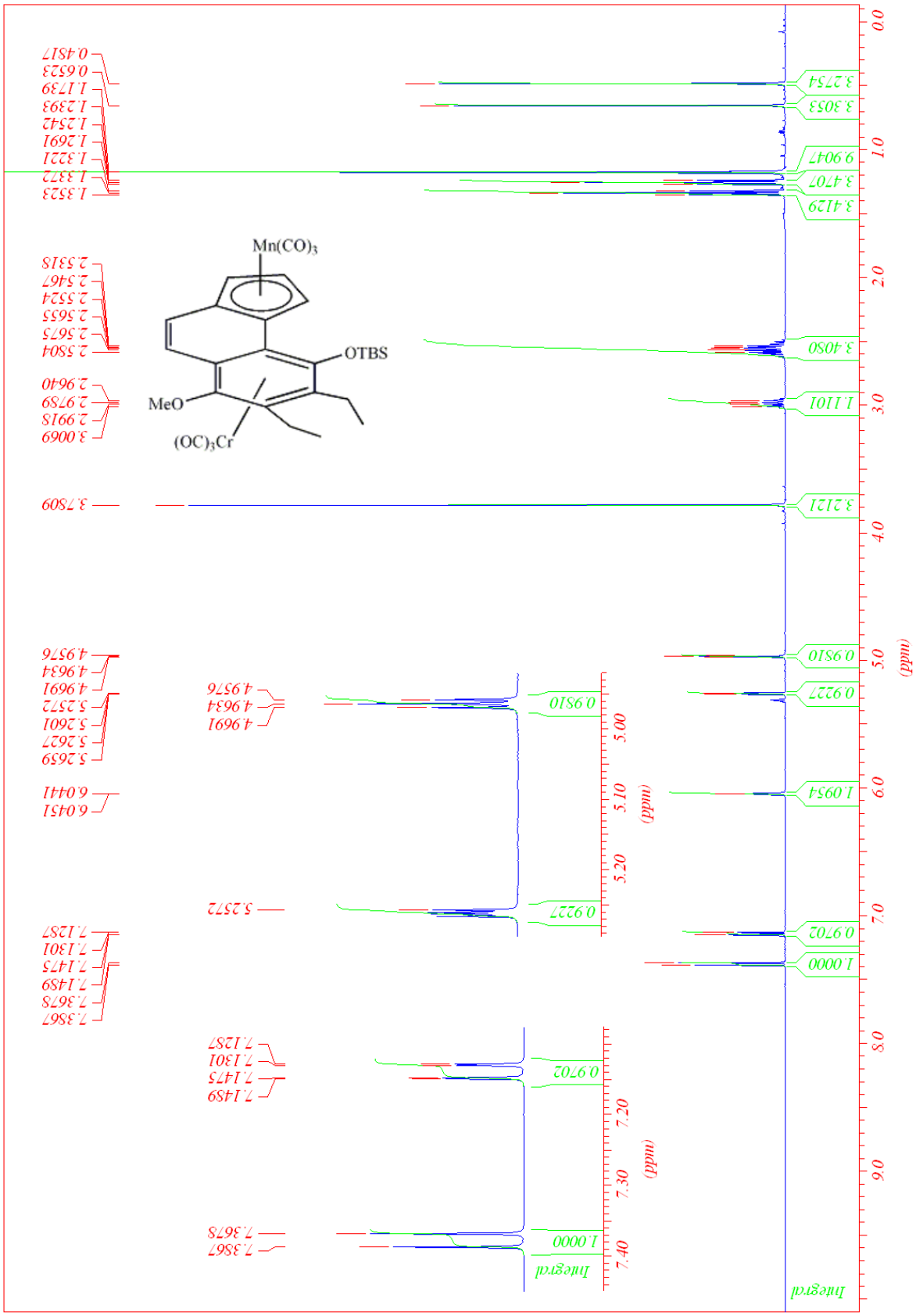
^{1}H-NMR Spectrum of complex 6



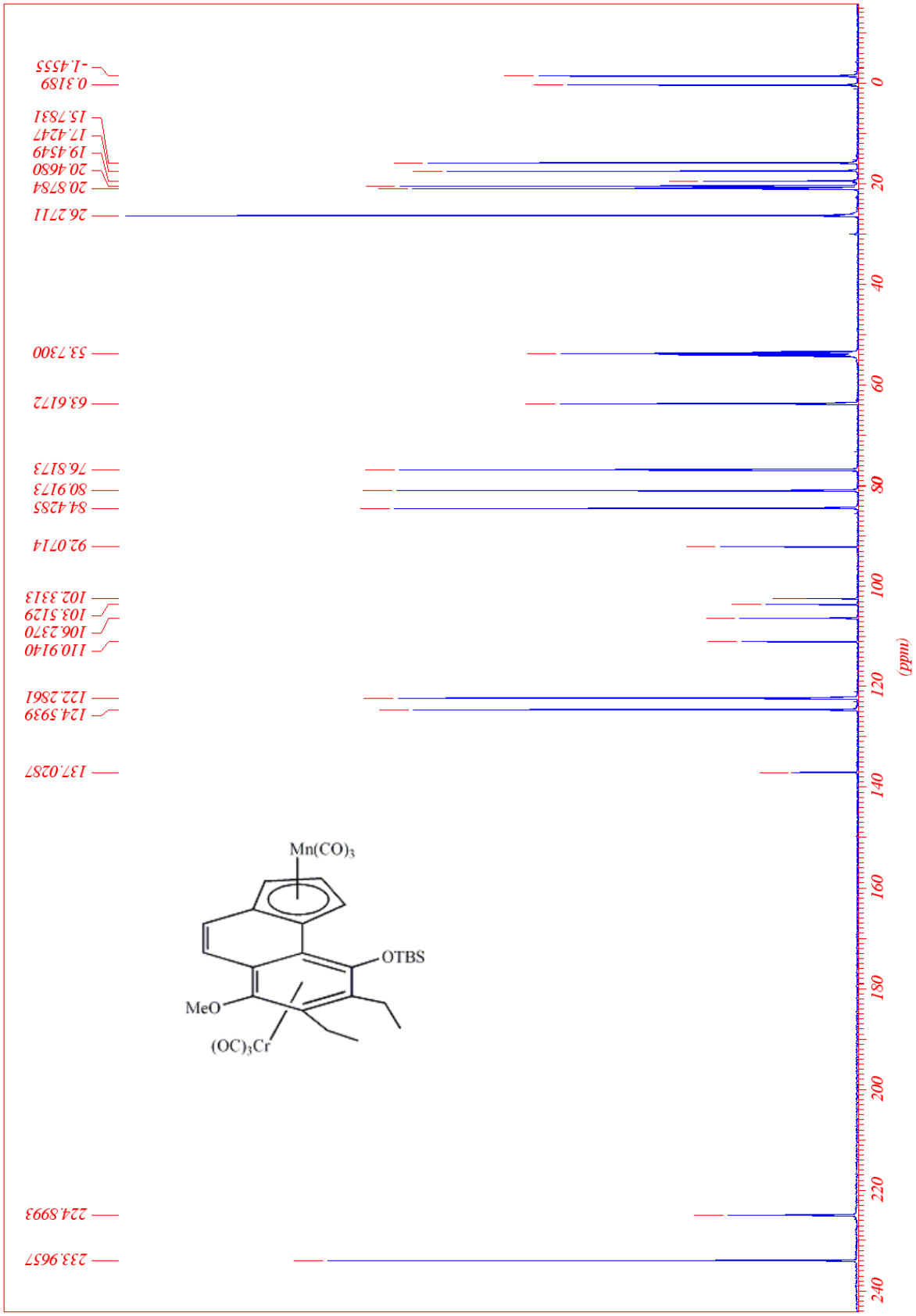
^{13}C-NMR spectrum of complex 6



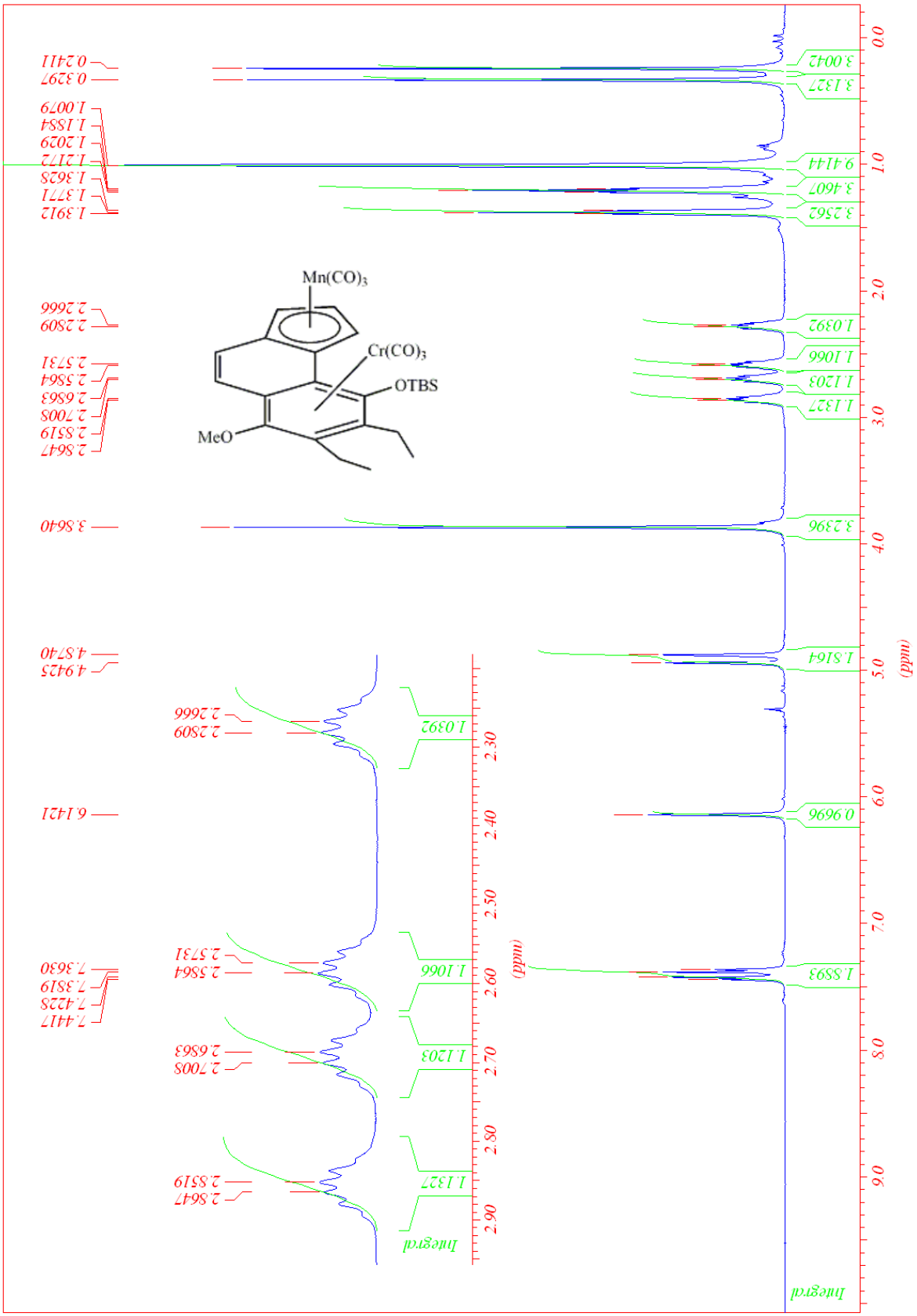
^{1}H-NMR Spectrum of complex 7



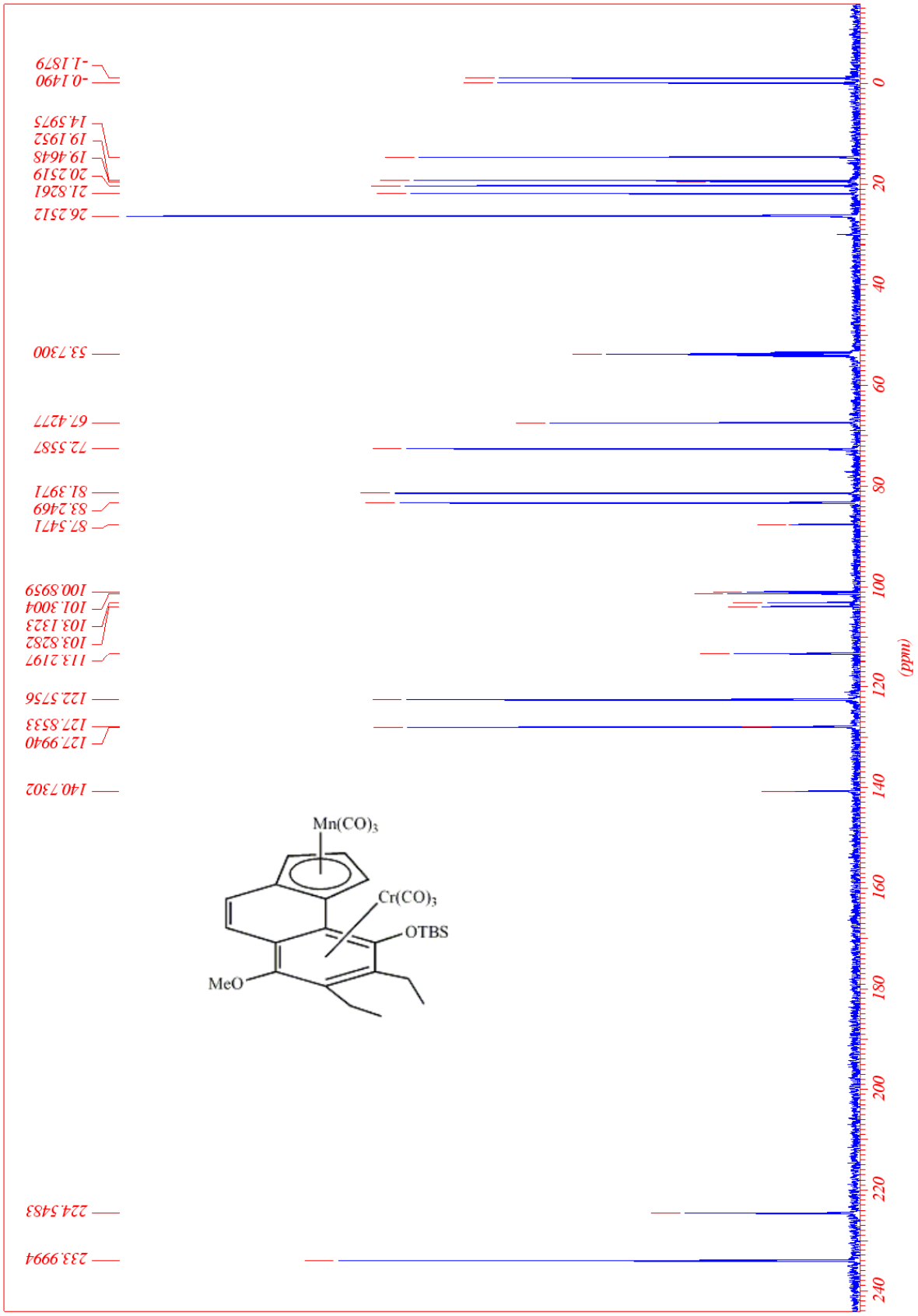
^{13}C-NMR spectrum of complex 7



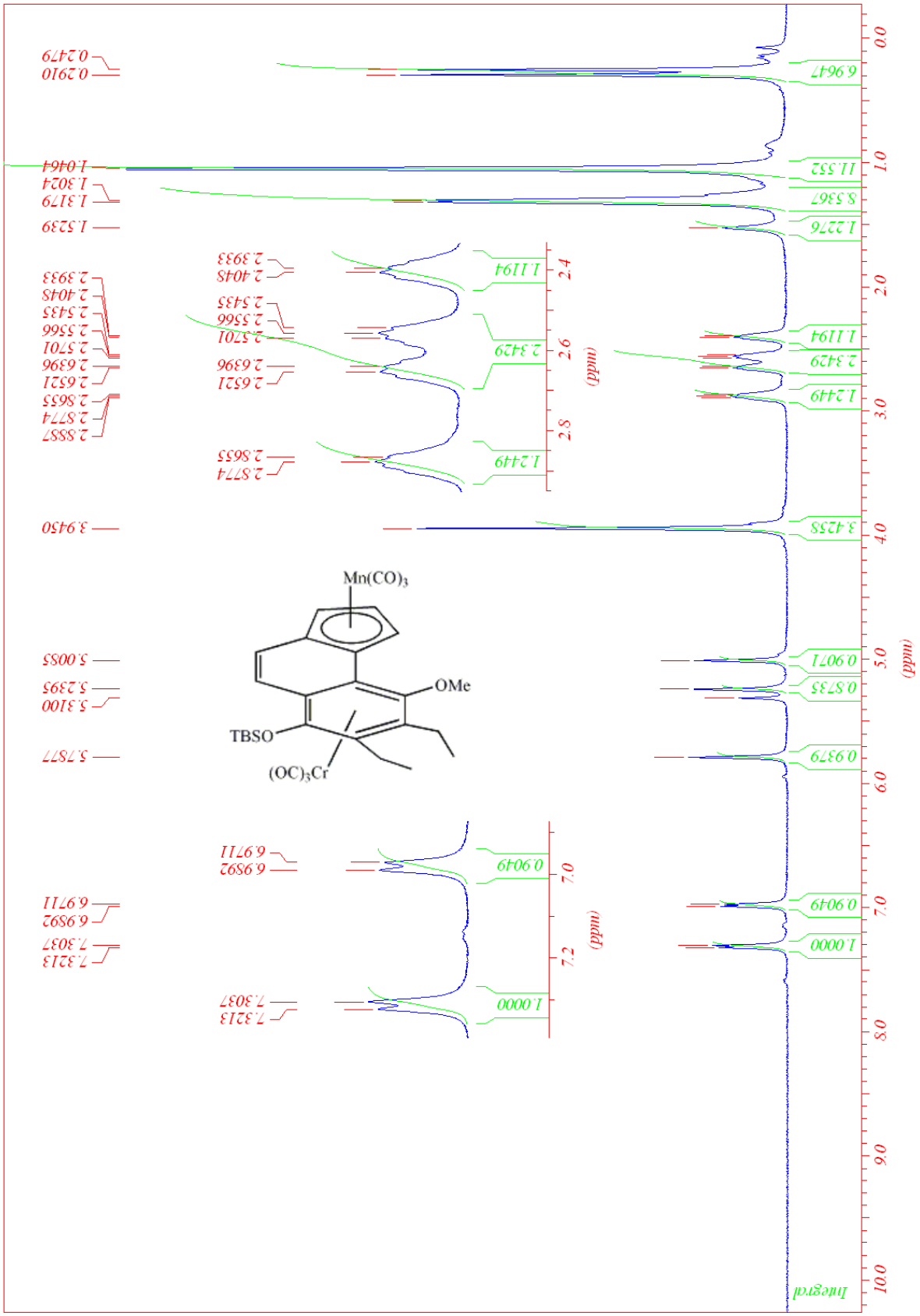
^{1}H-NMR Spectrum of complex 8



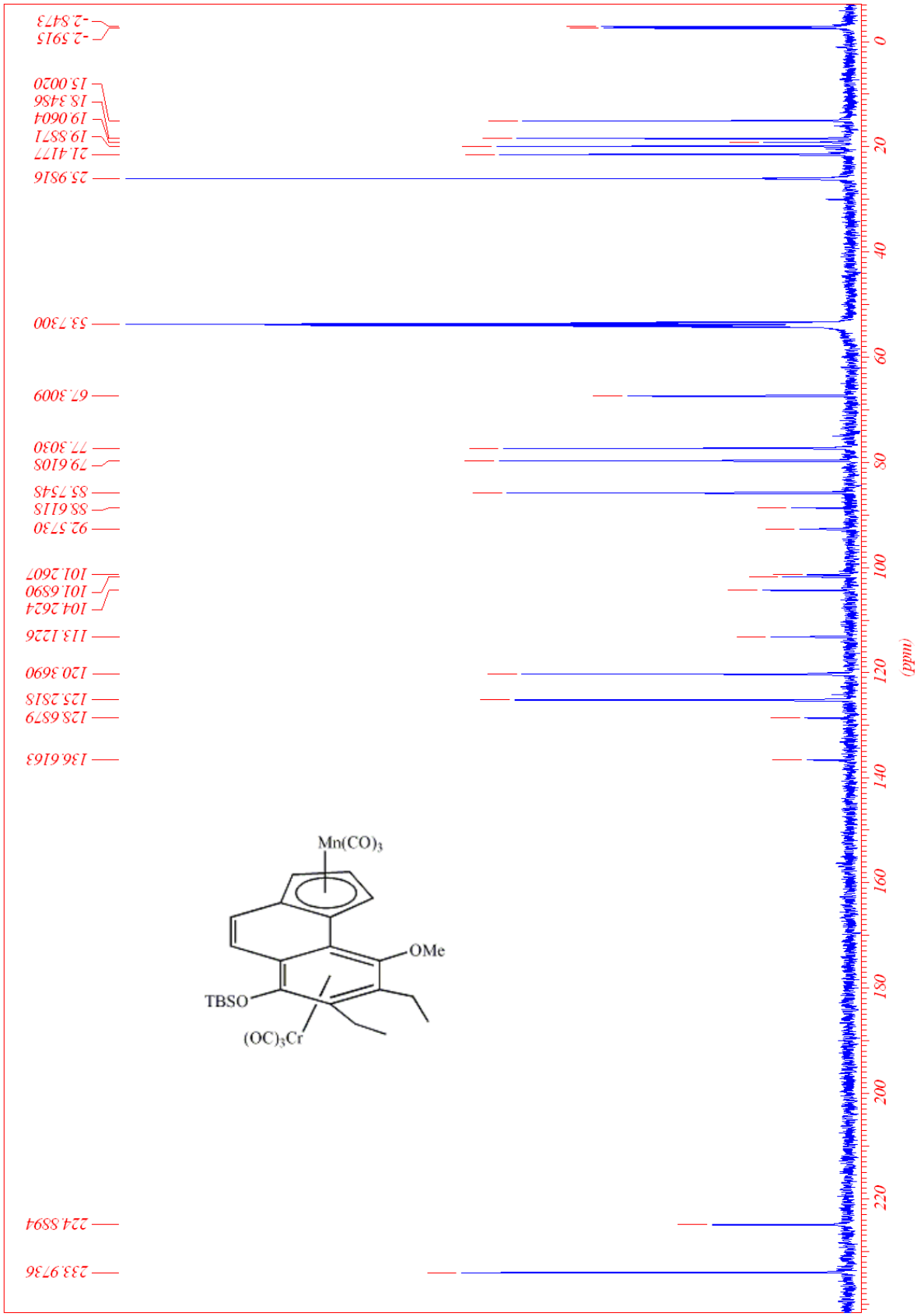
^{13}C-NMR spectrum of complex 8



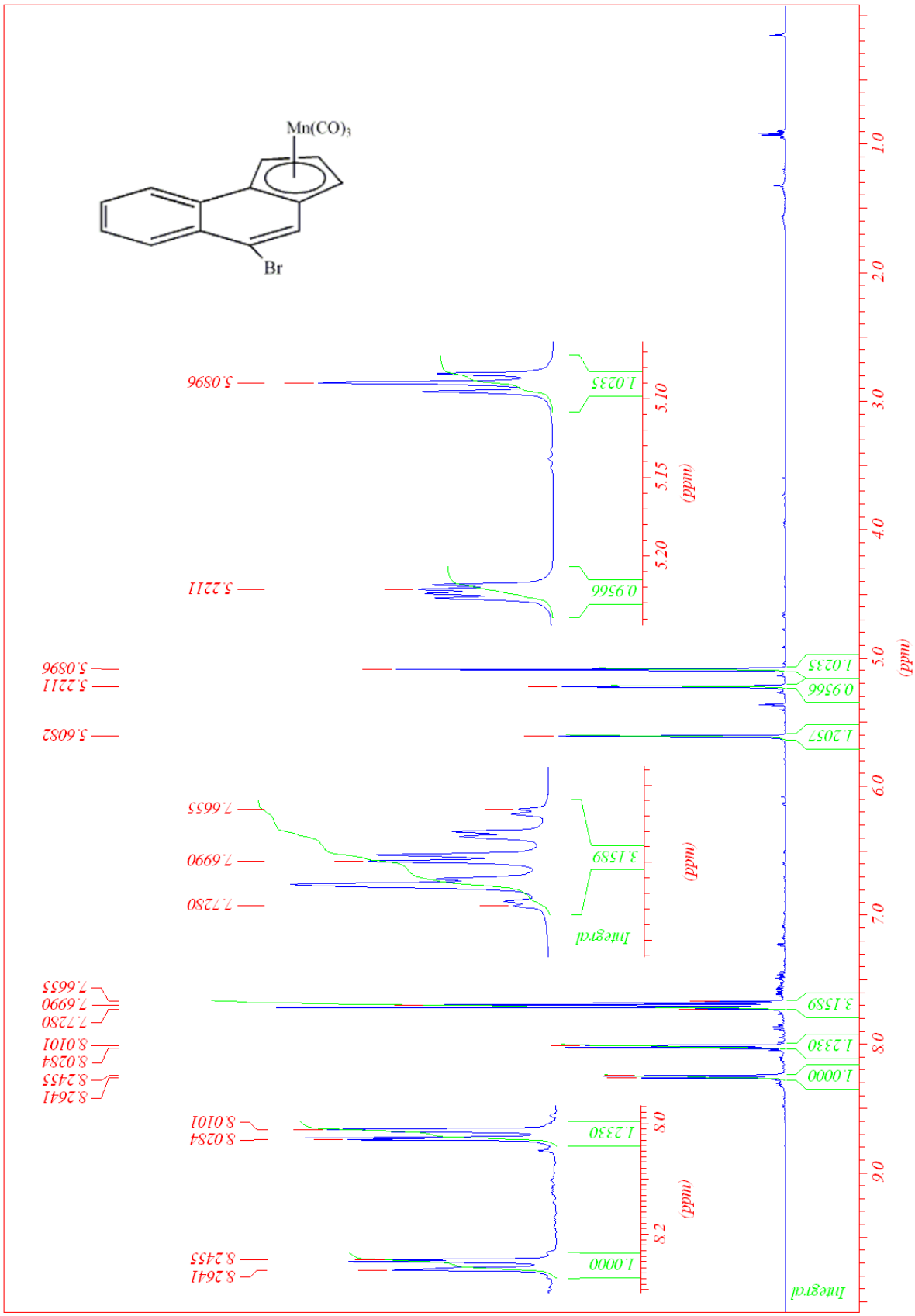
^{1}H-NMR Spectrum of complex 9



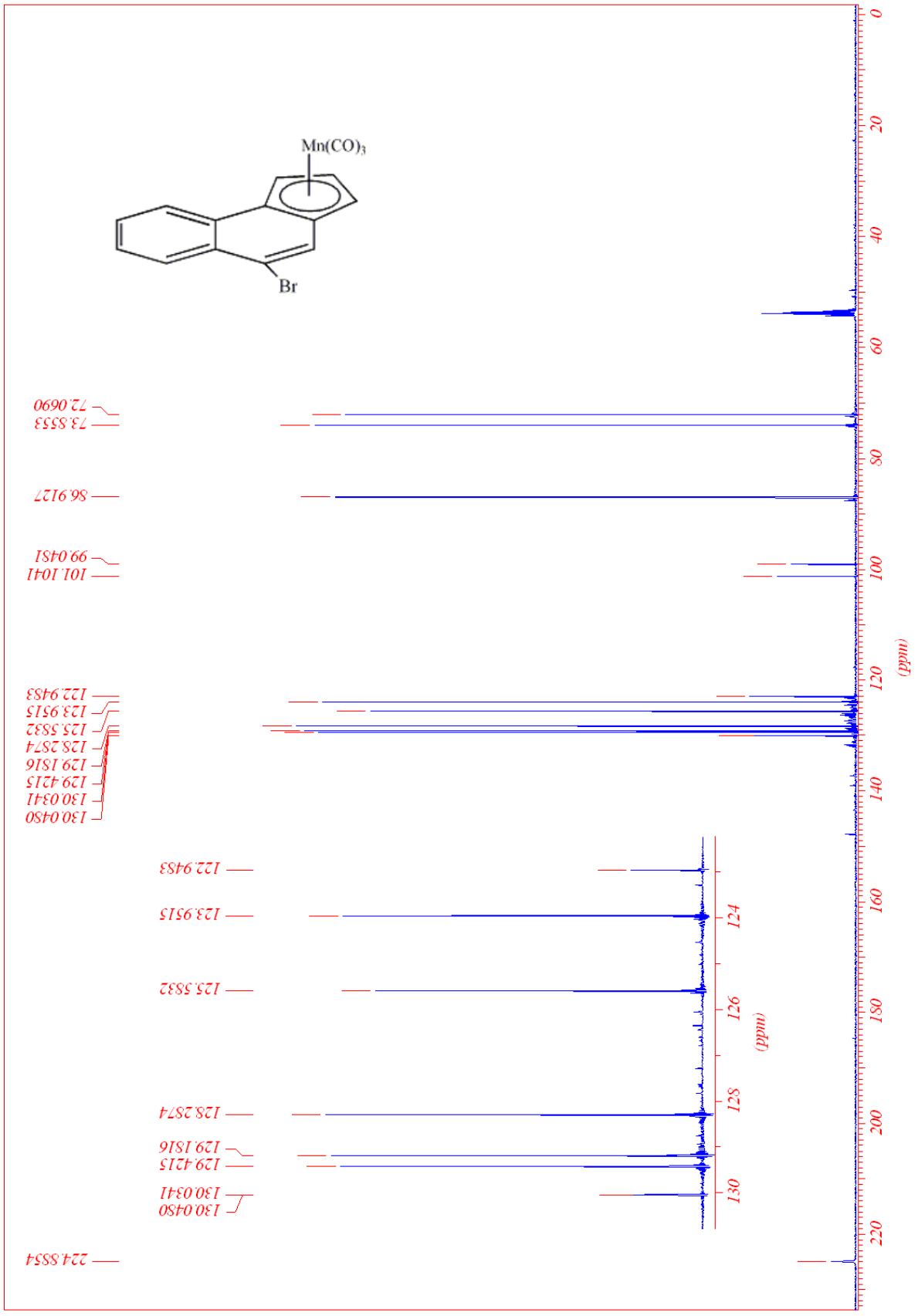
^{13}C-NMR spectrum of complex 9



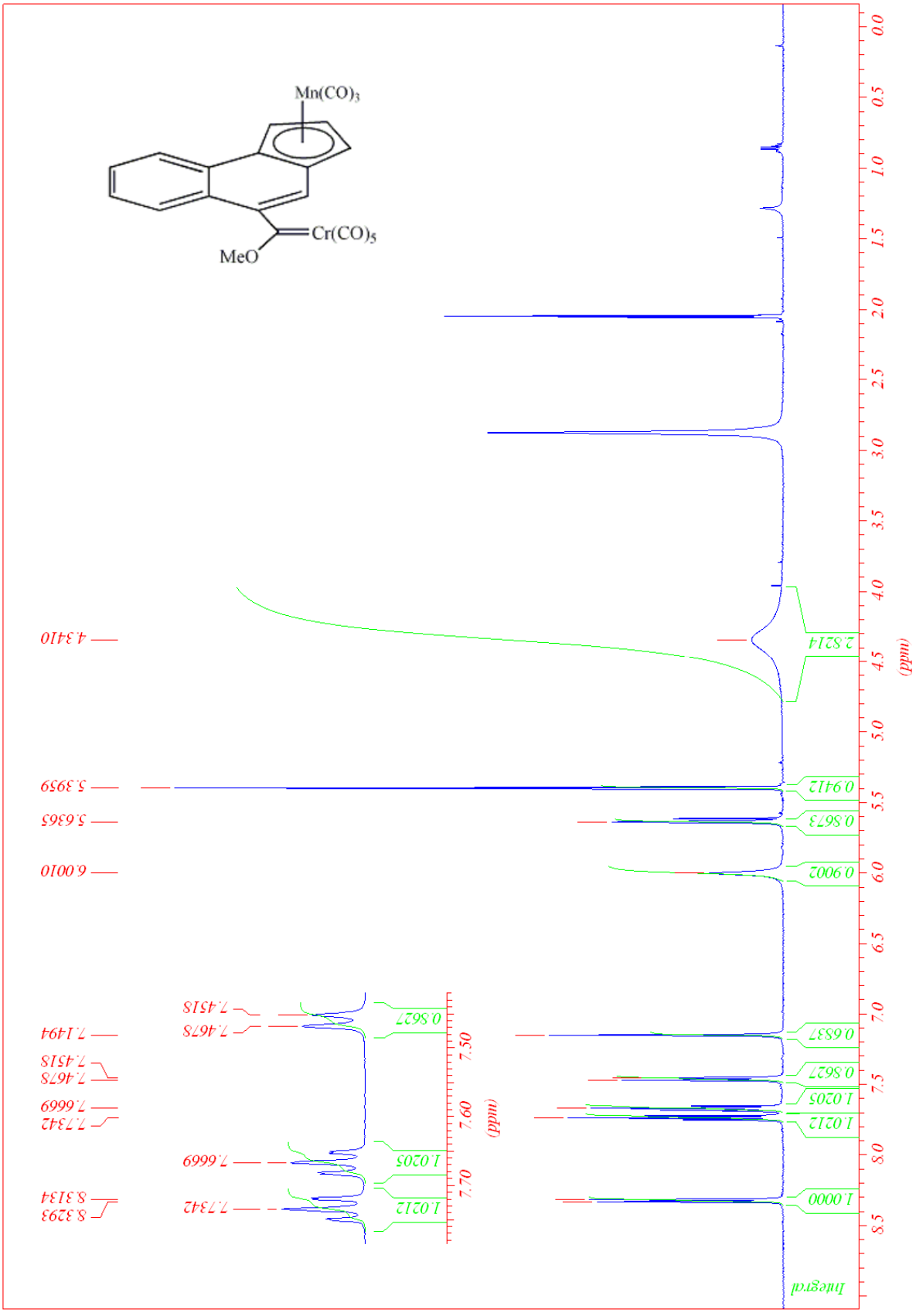
[1]H-NMR Spectrum of complex 15



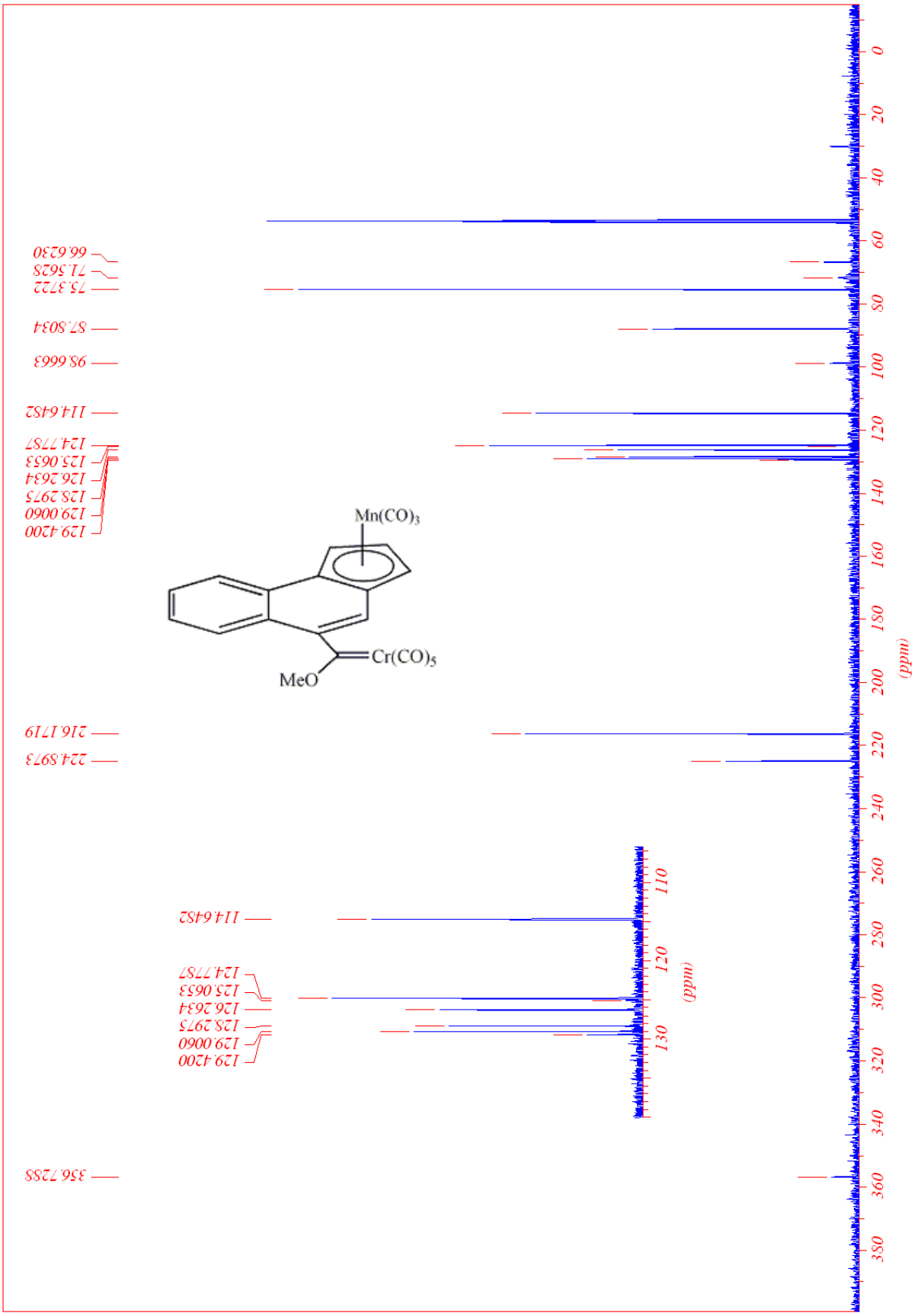
^{13}C-NMR spectrum of complex 15



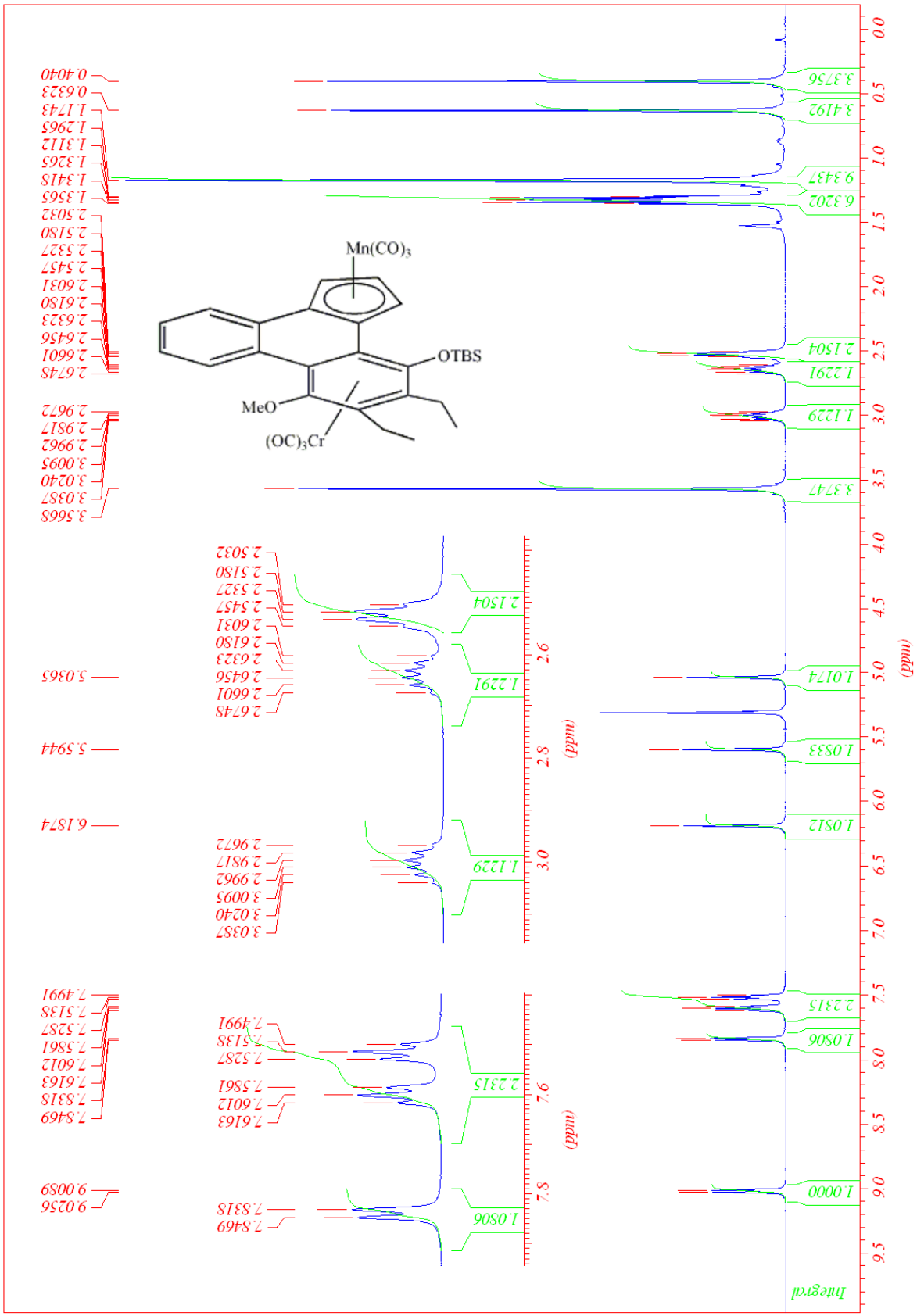
^{1}H-NMR Spectrum of complex 16



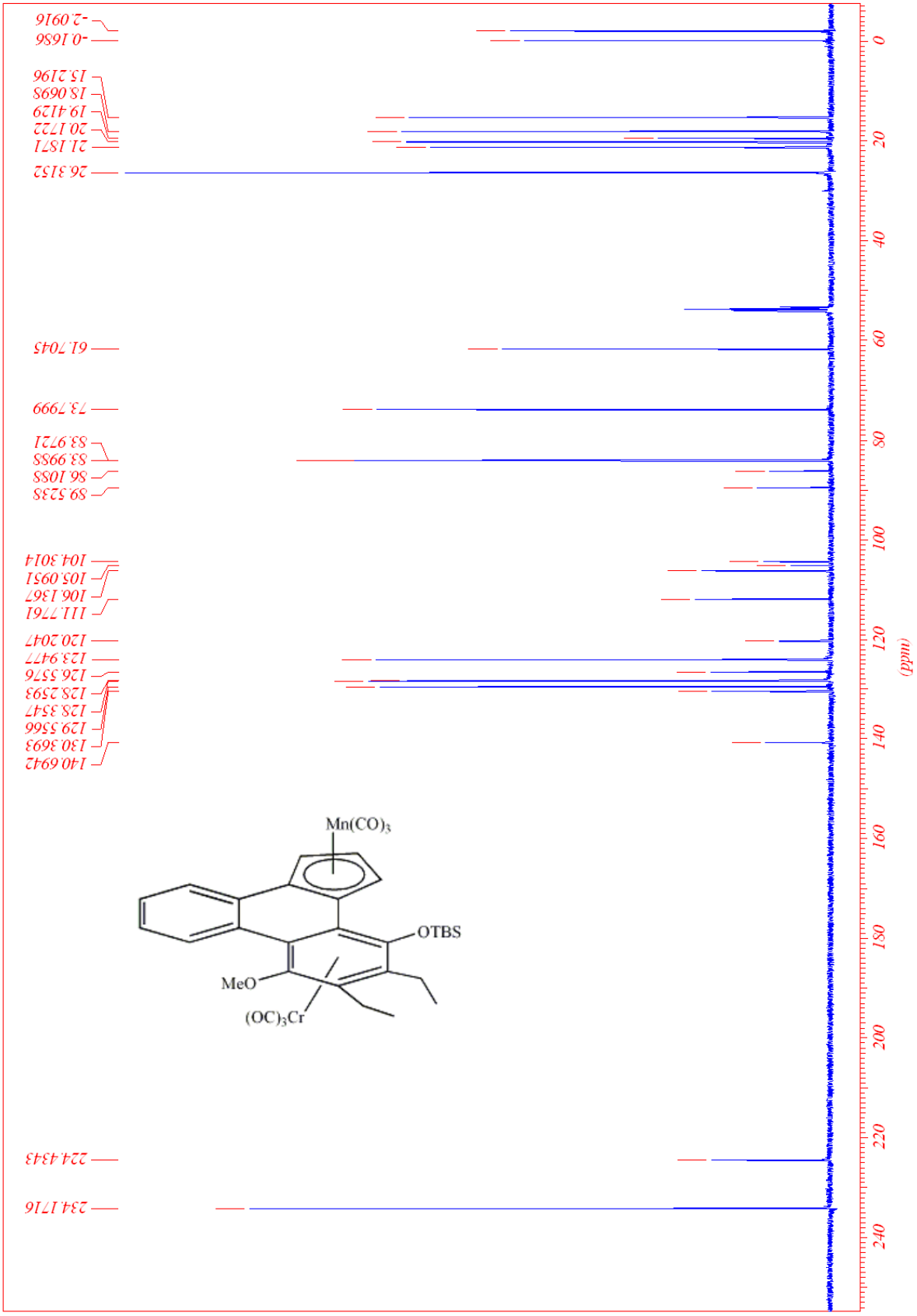
^{13}C-NMR spectrum of complex 16



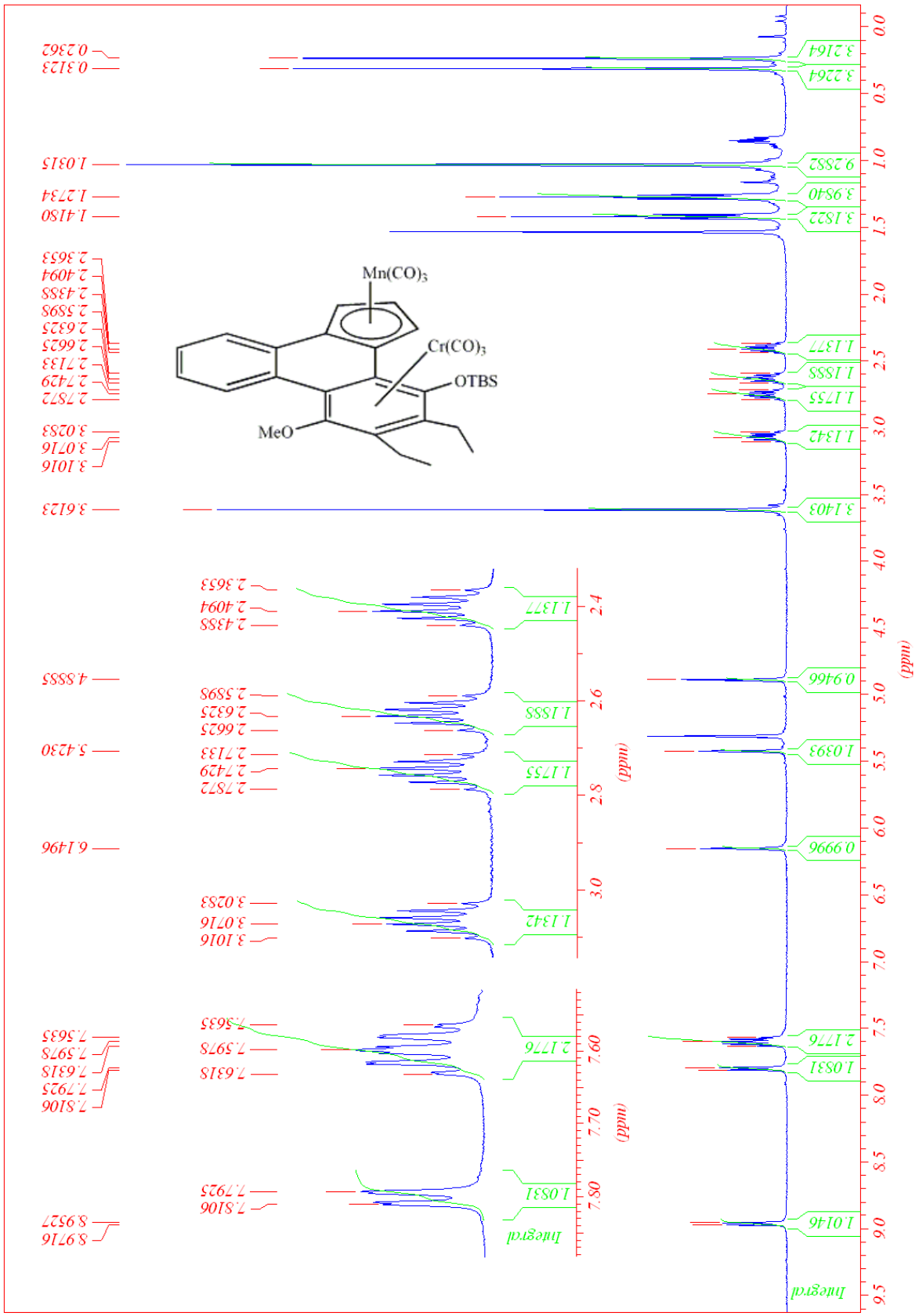
[1]H-NMR Spectrum of complex 17



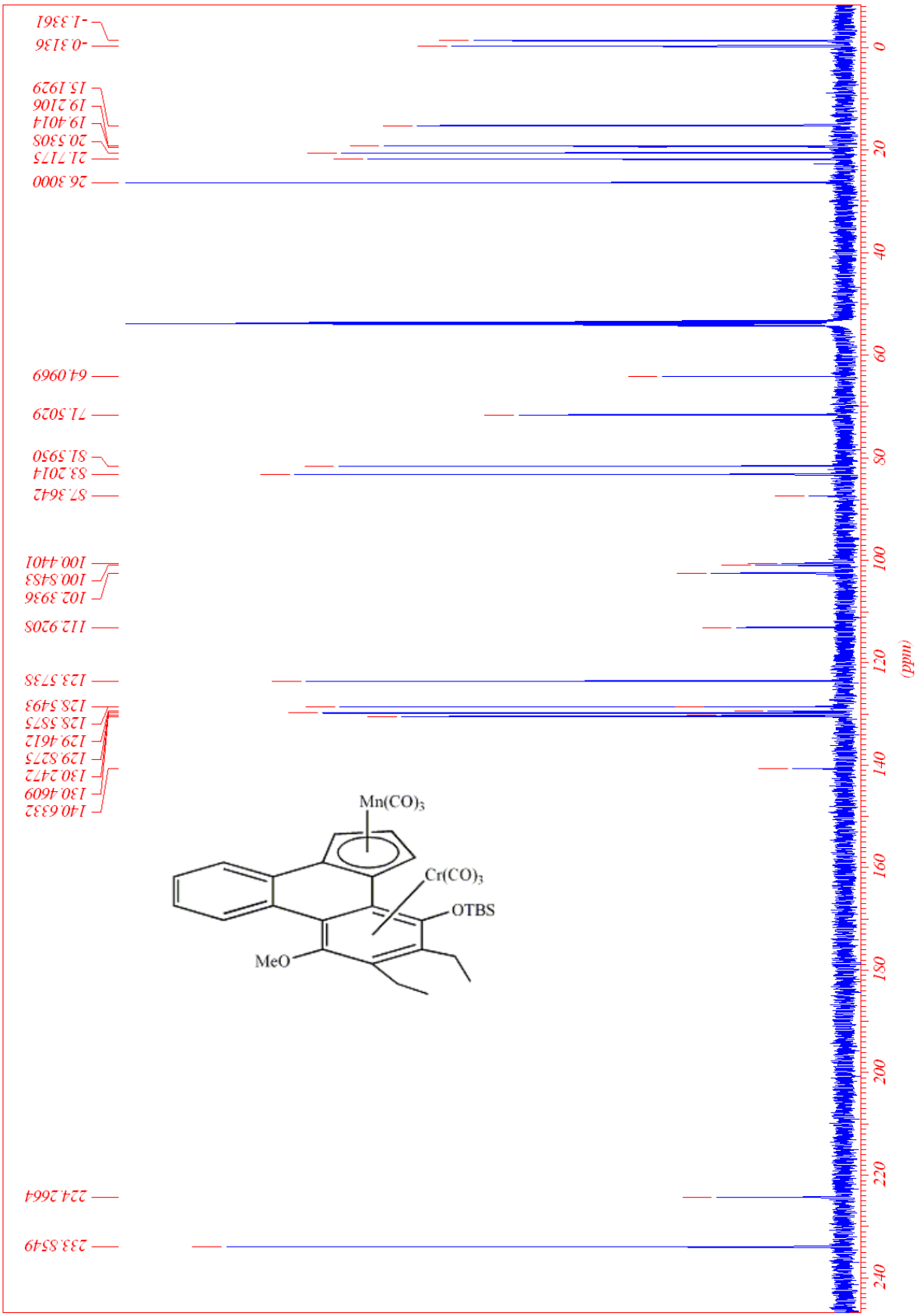
^{13}C-NMR spectrum of complex 17



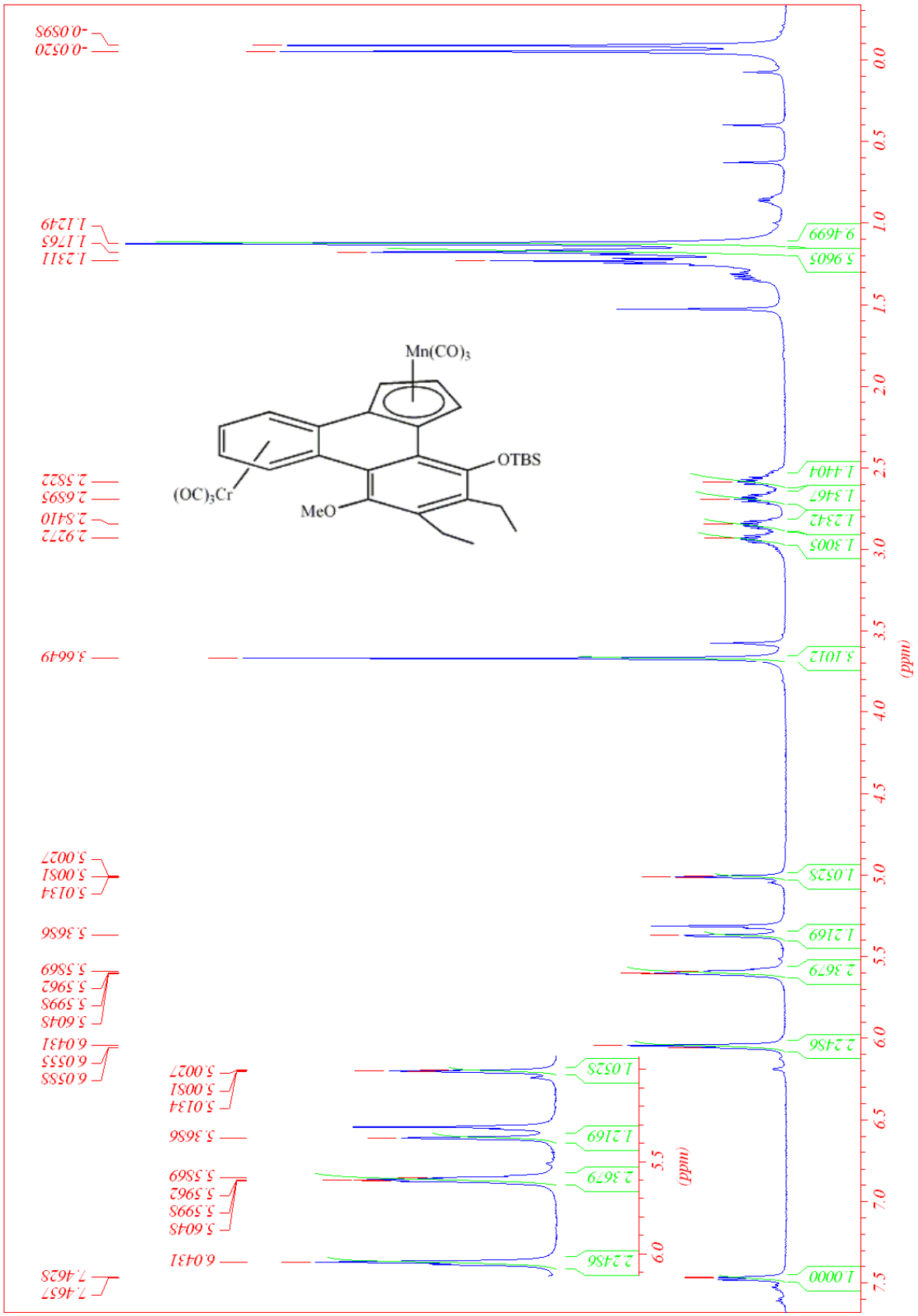
^{1}H-NMR Spectrum of complex 18



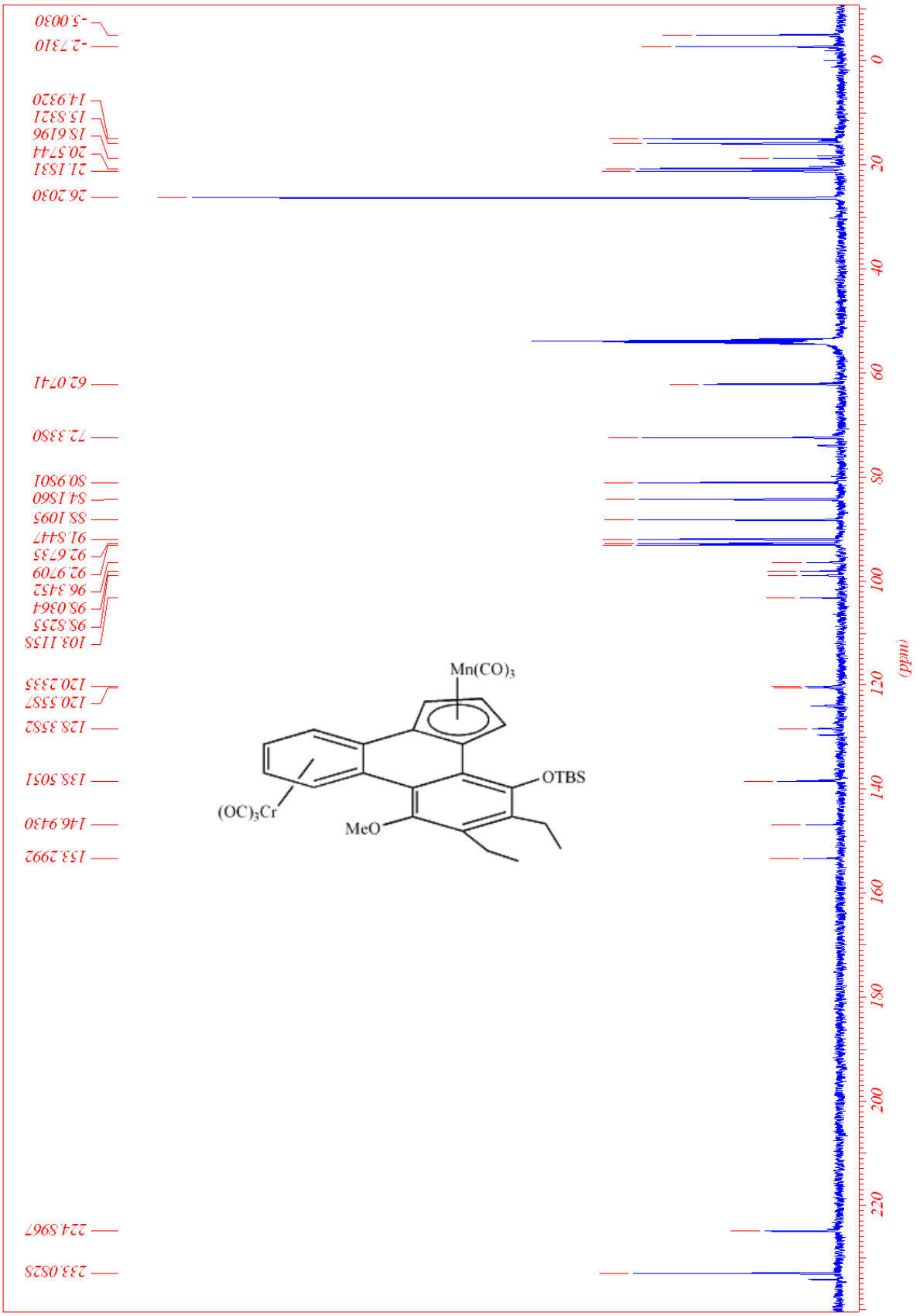
^{13}C-NMR spectrum of complex 18



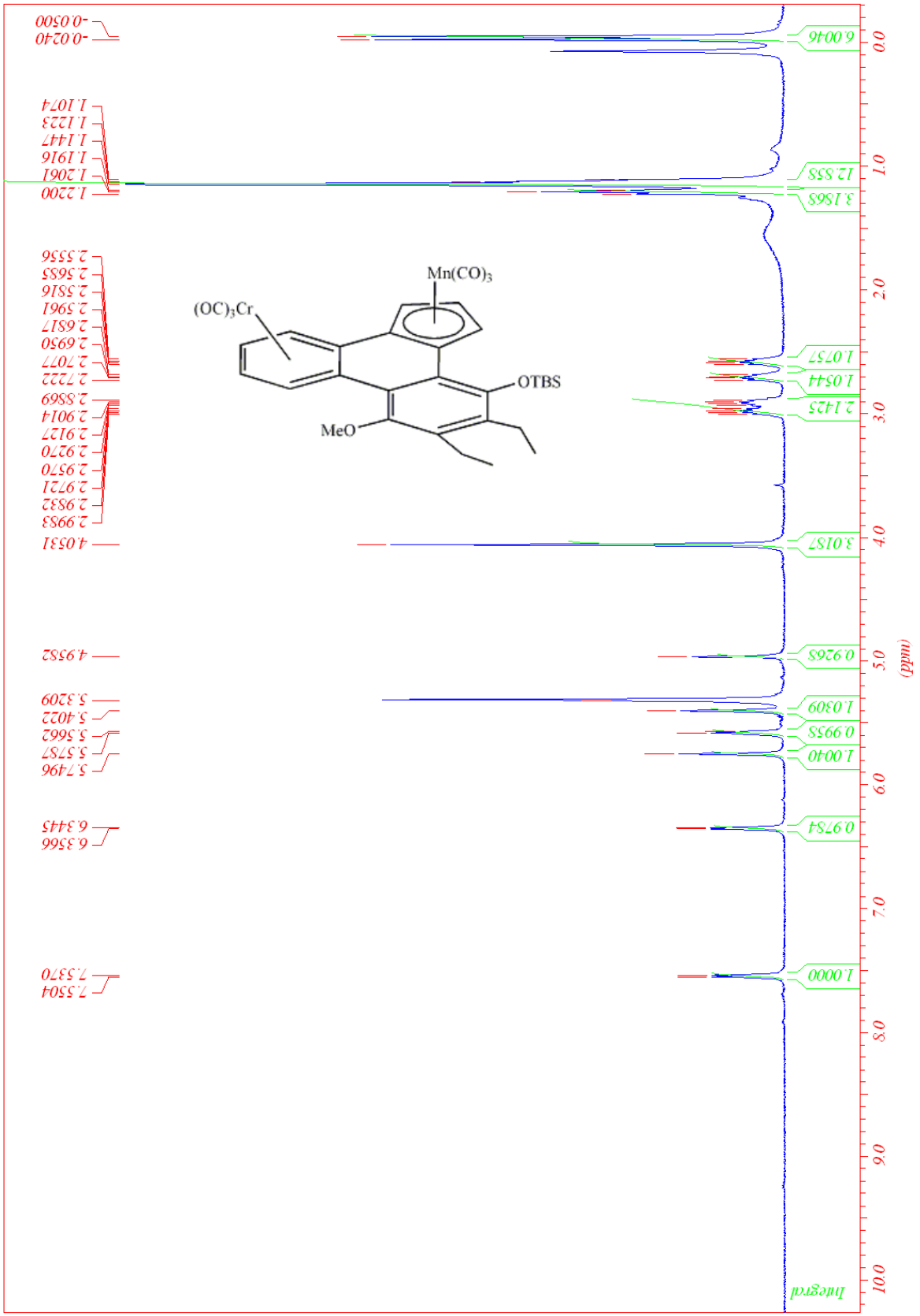
^{1}H-NMR Spectrum of complex 19



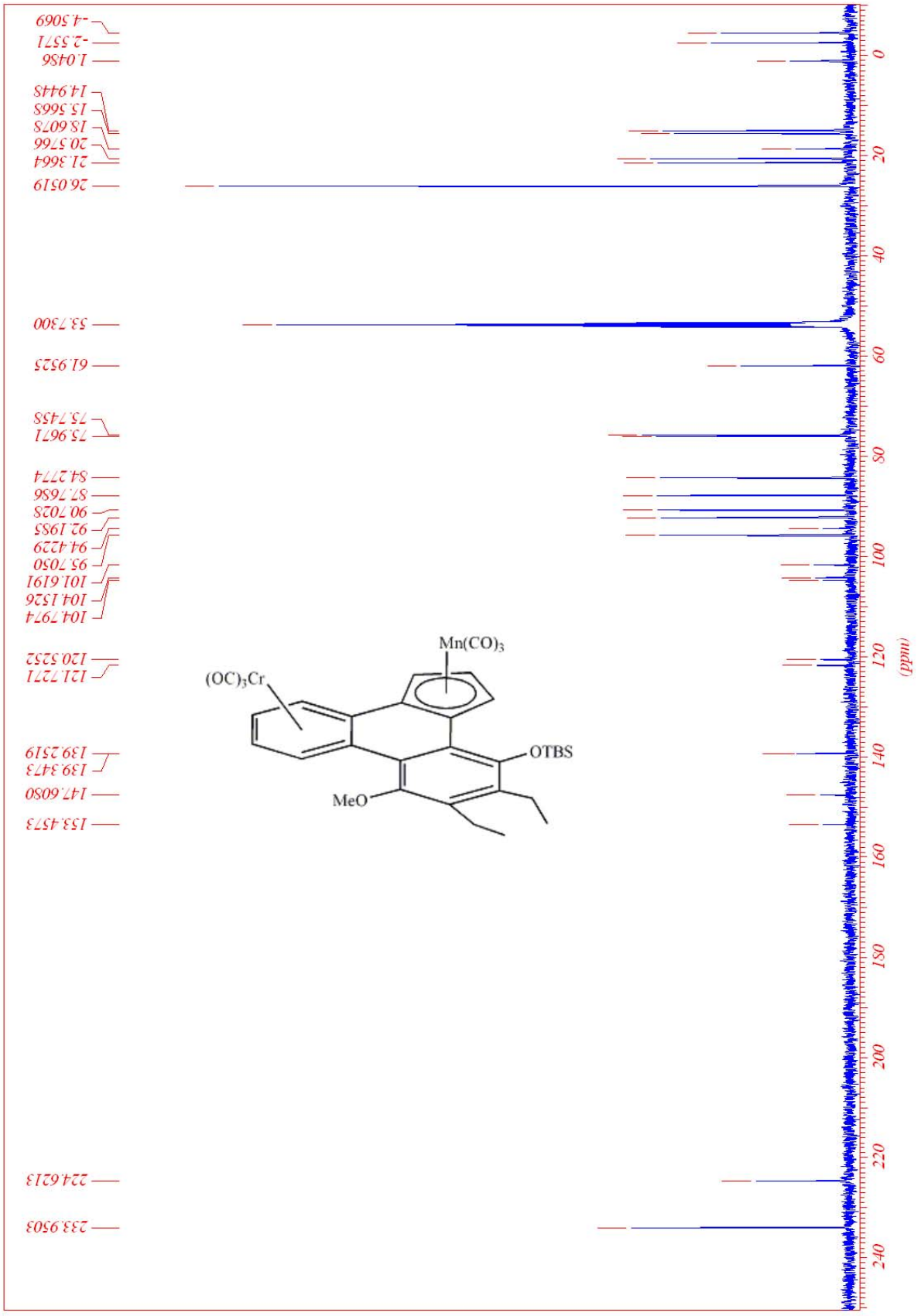
^{13}C-NMR spectrum of complex 19



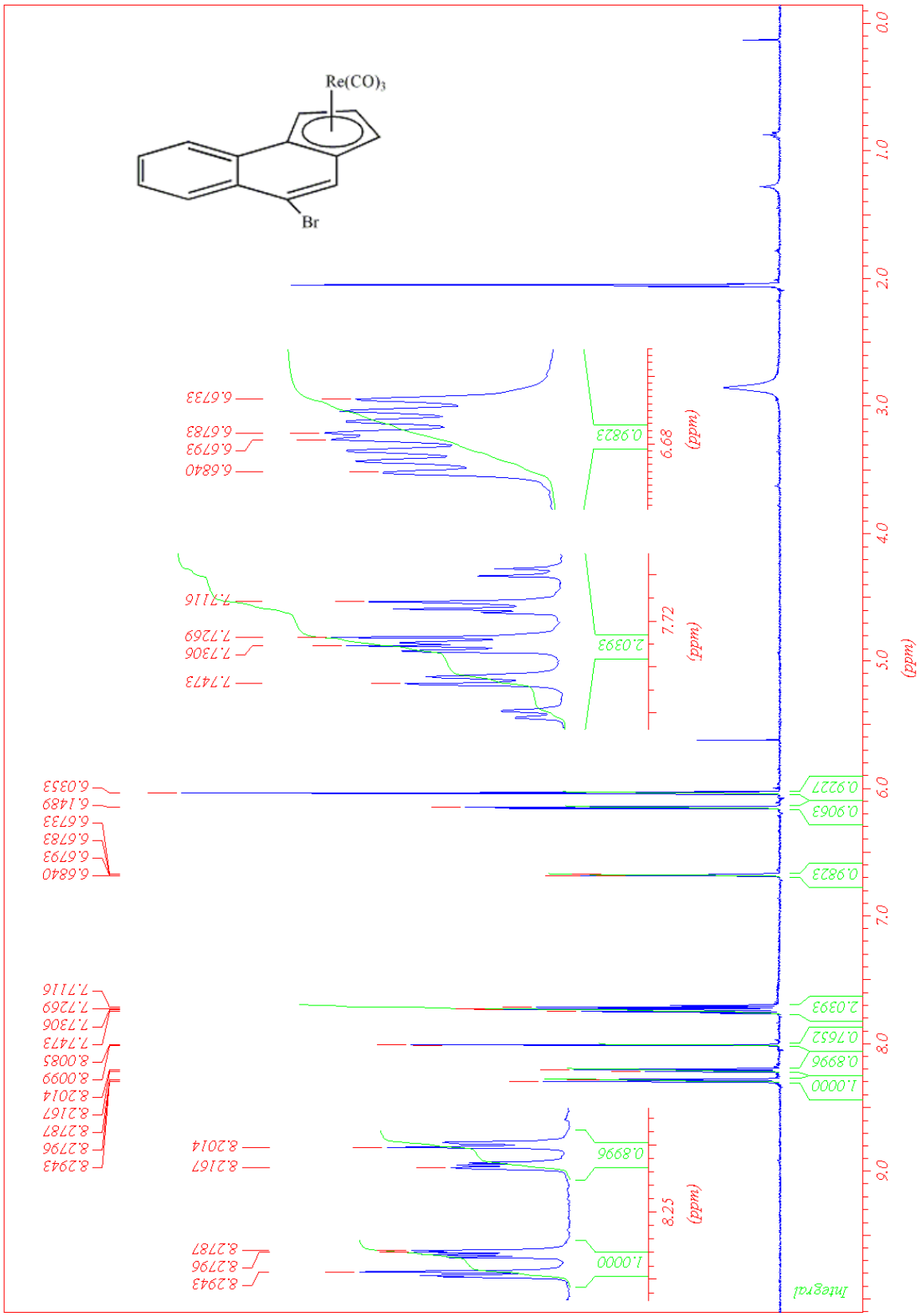
[1]H-NMR Spectrum of complex 20



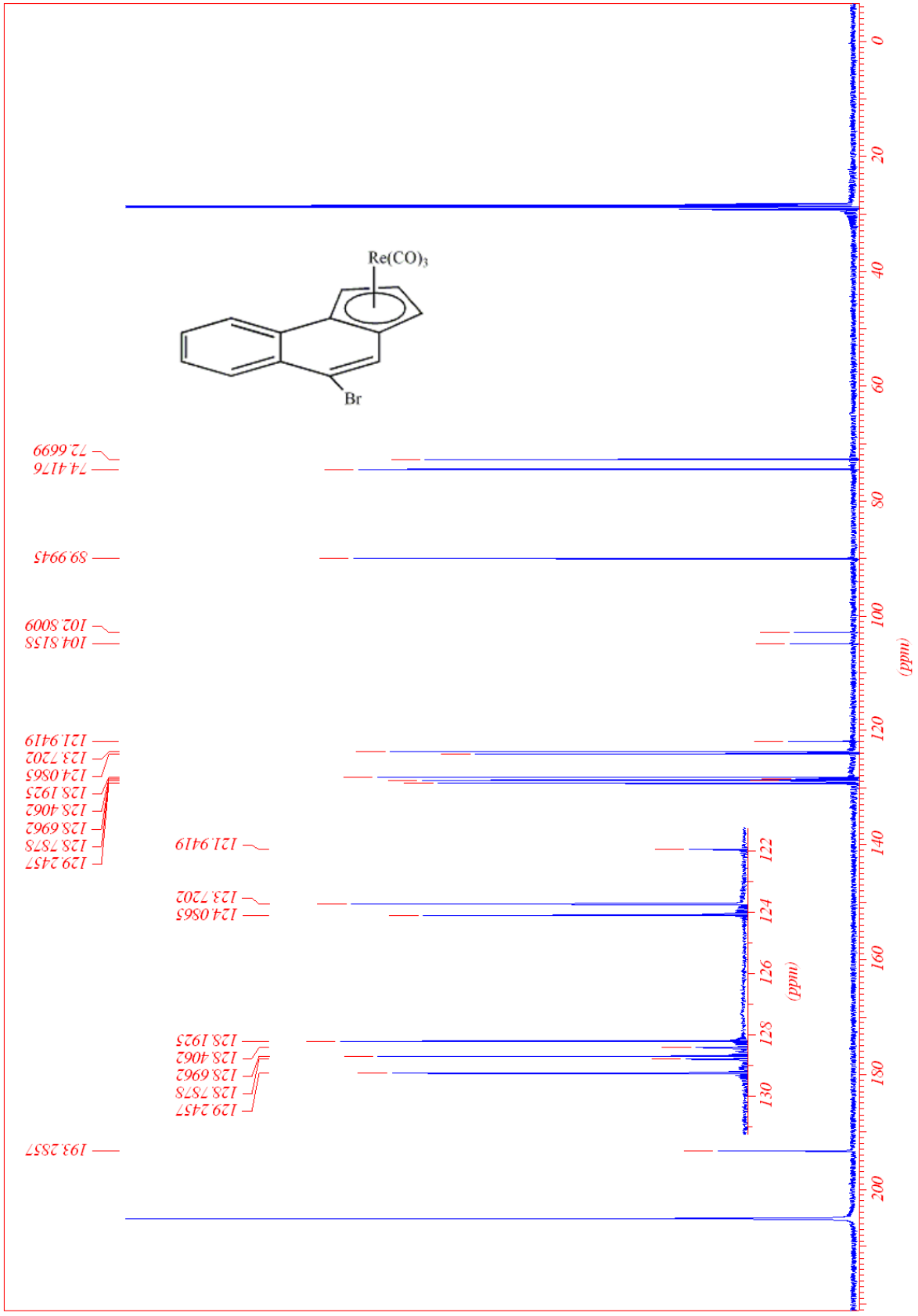
^{13}C-NMR spectrum of complex 20



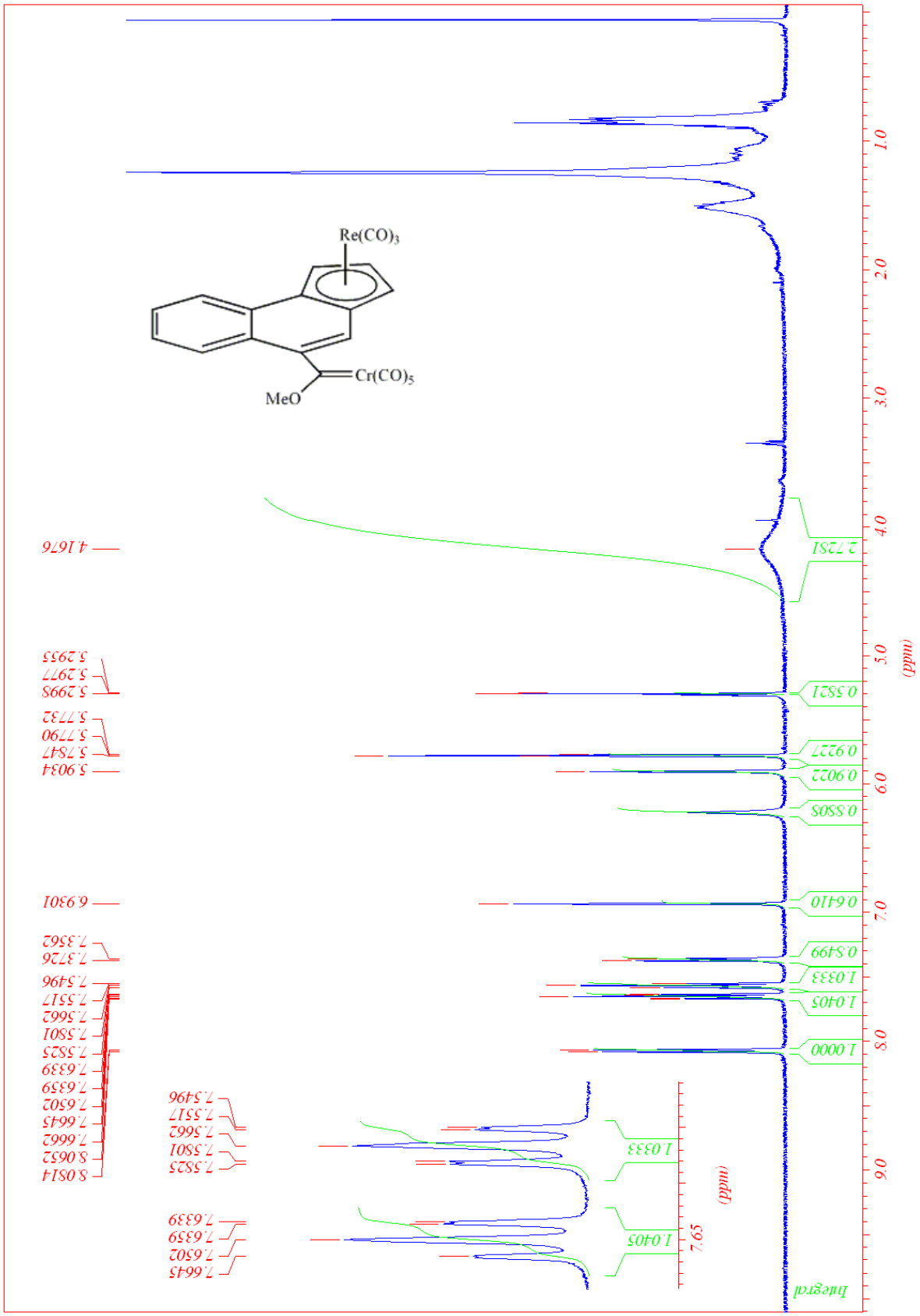
^{1}H-NMR Spectrum of complex 22



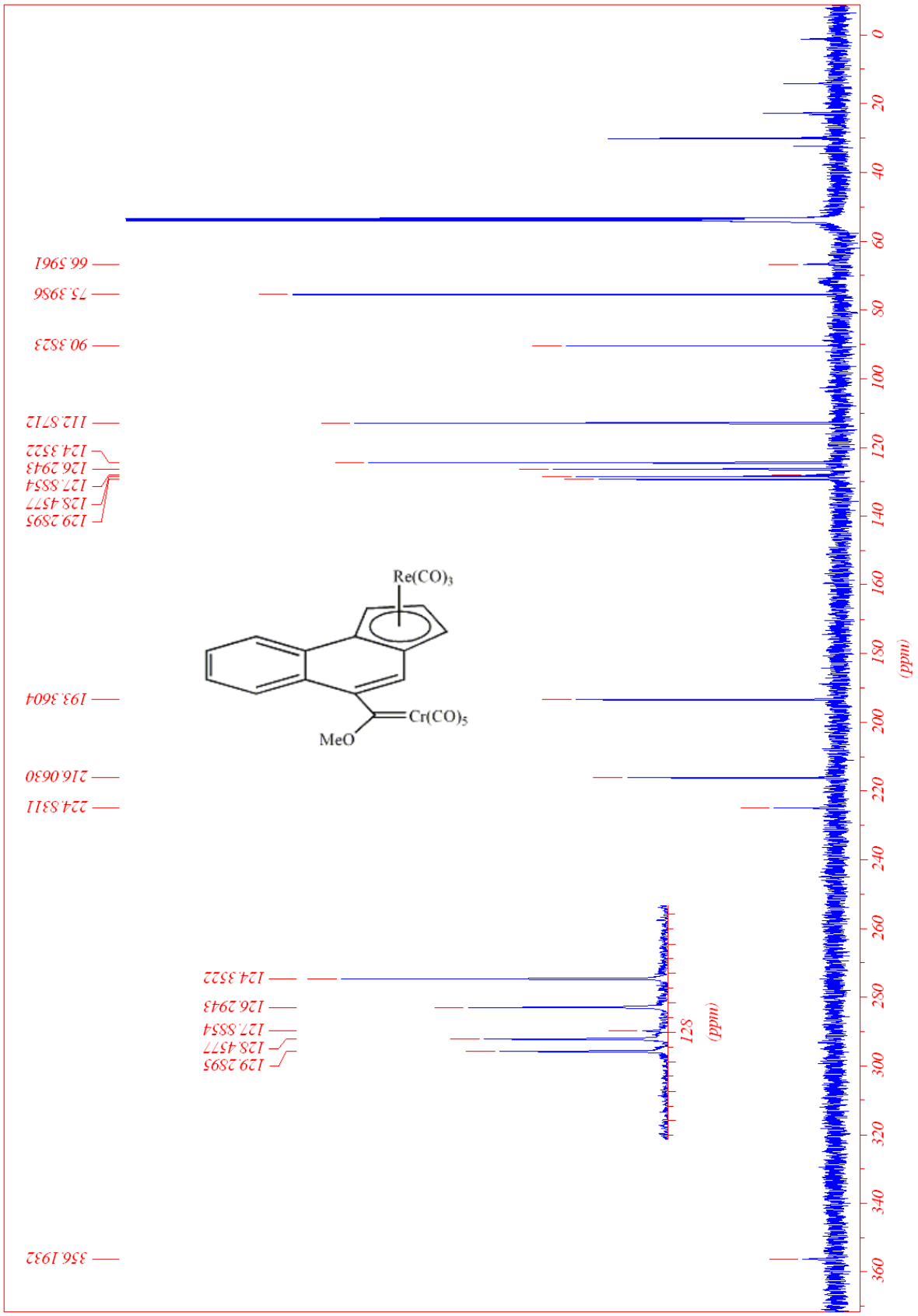
^{13}C-NMR spectrum of complex 22



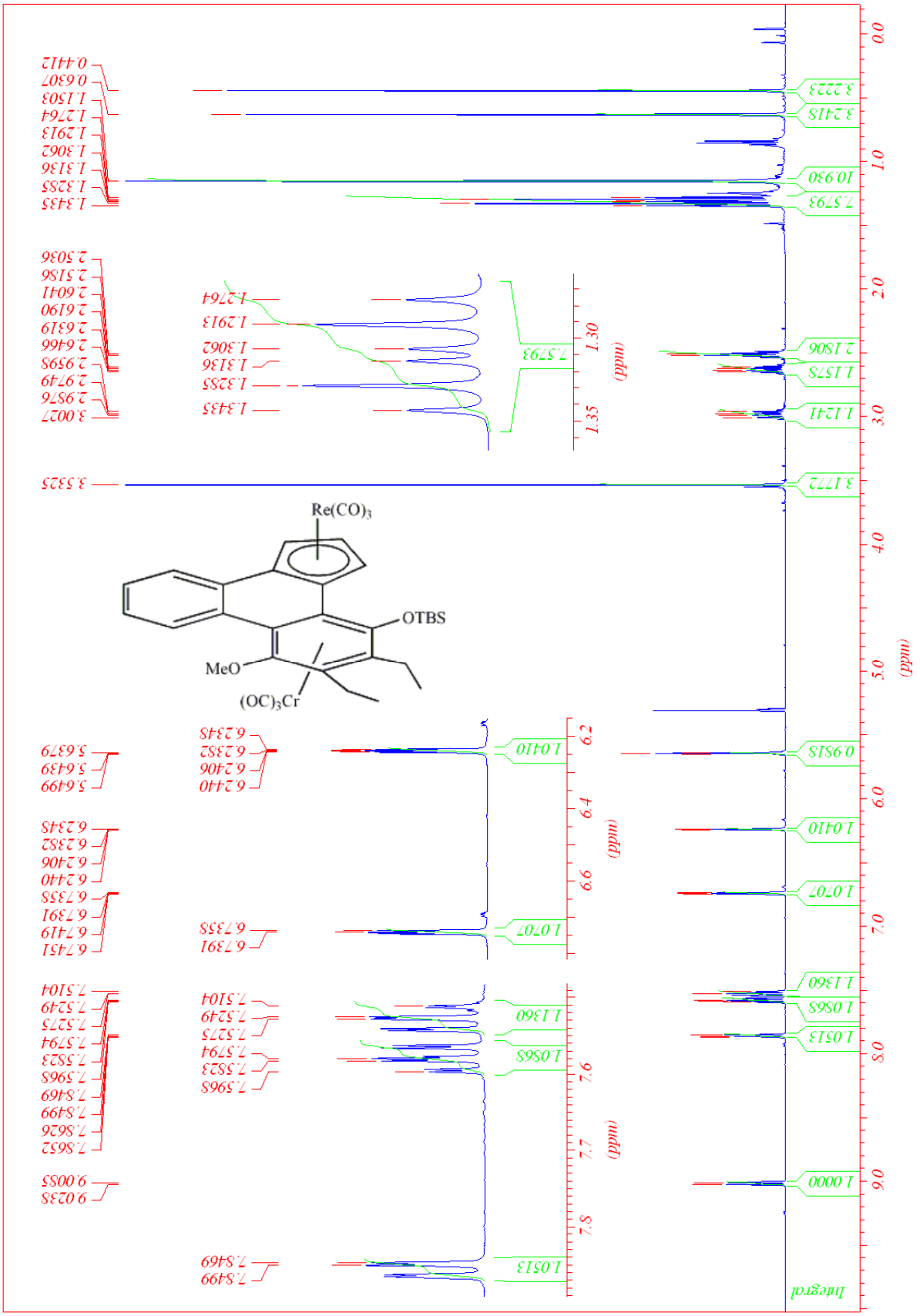
[1]H-NMR Spectrum of complex 23



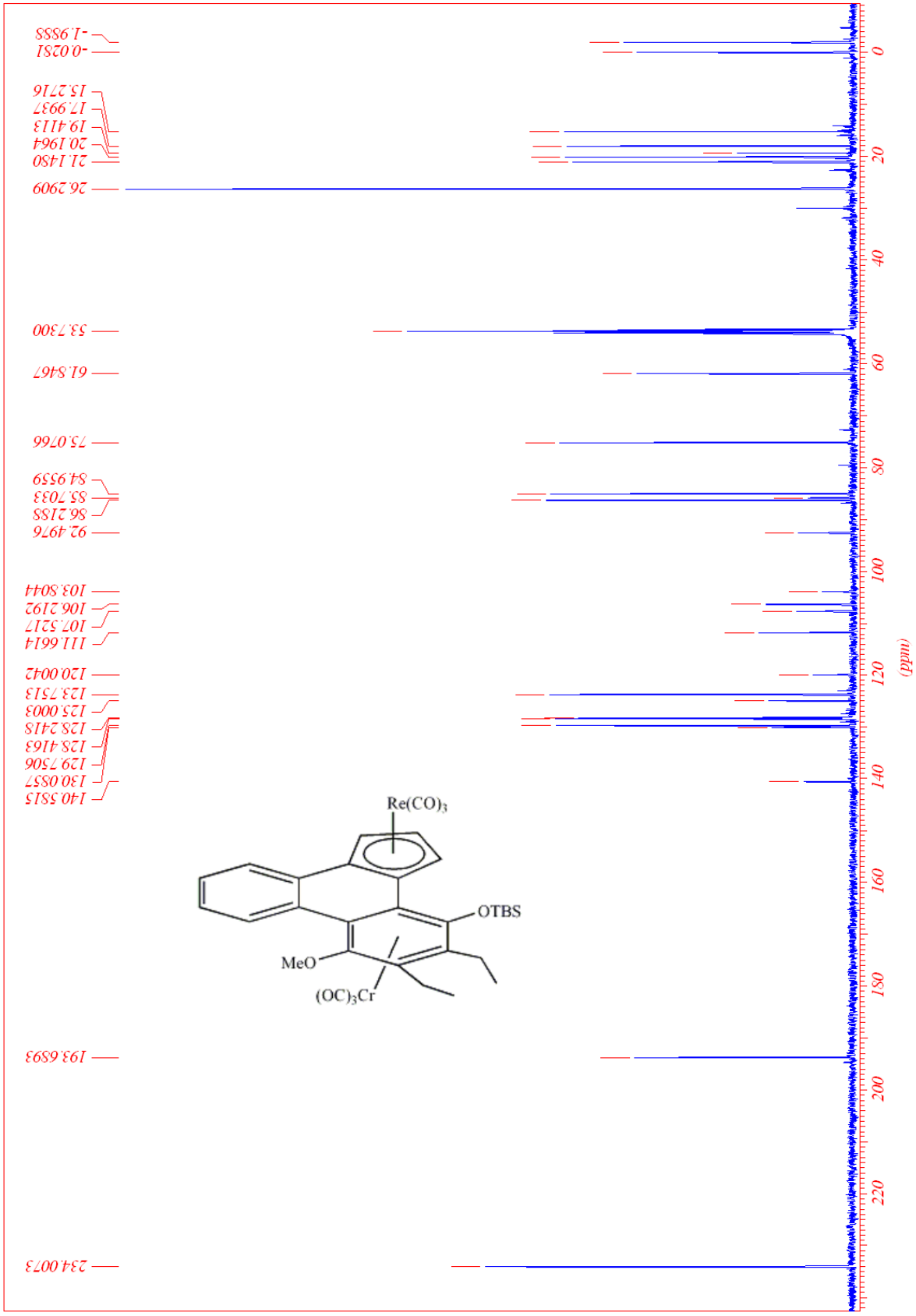
^{13}C-NMR spectrum of complex 23



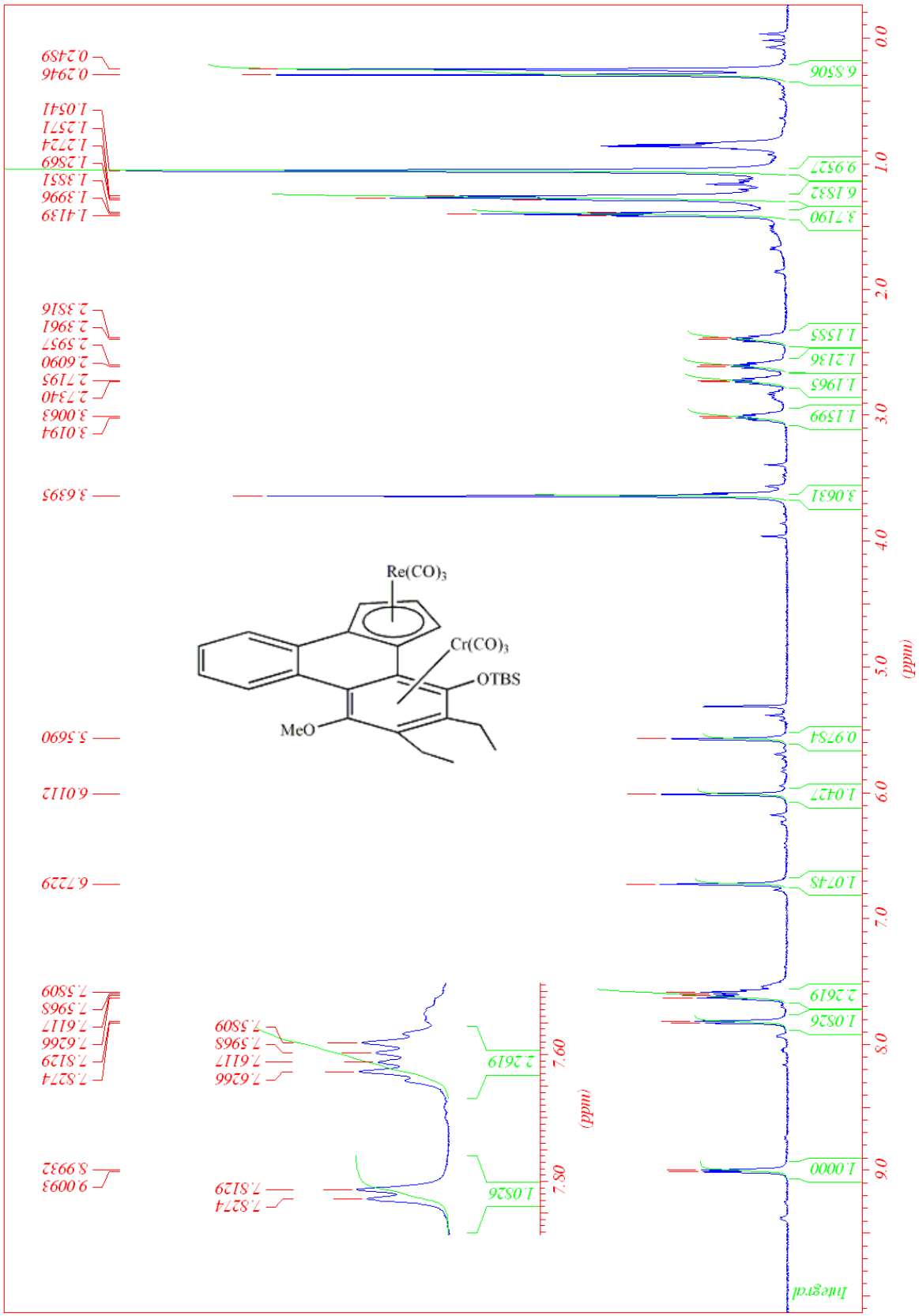
^{1}H-NMR Spectrum of complex 24



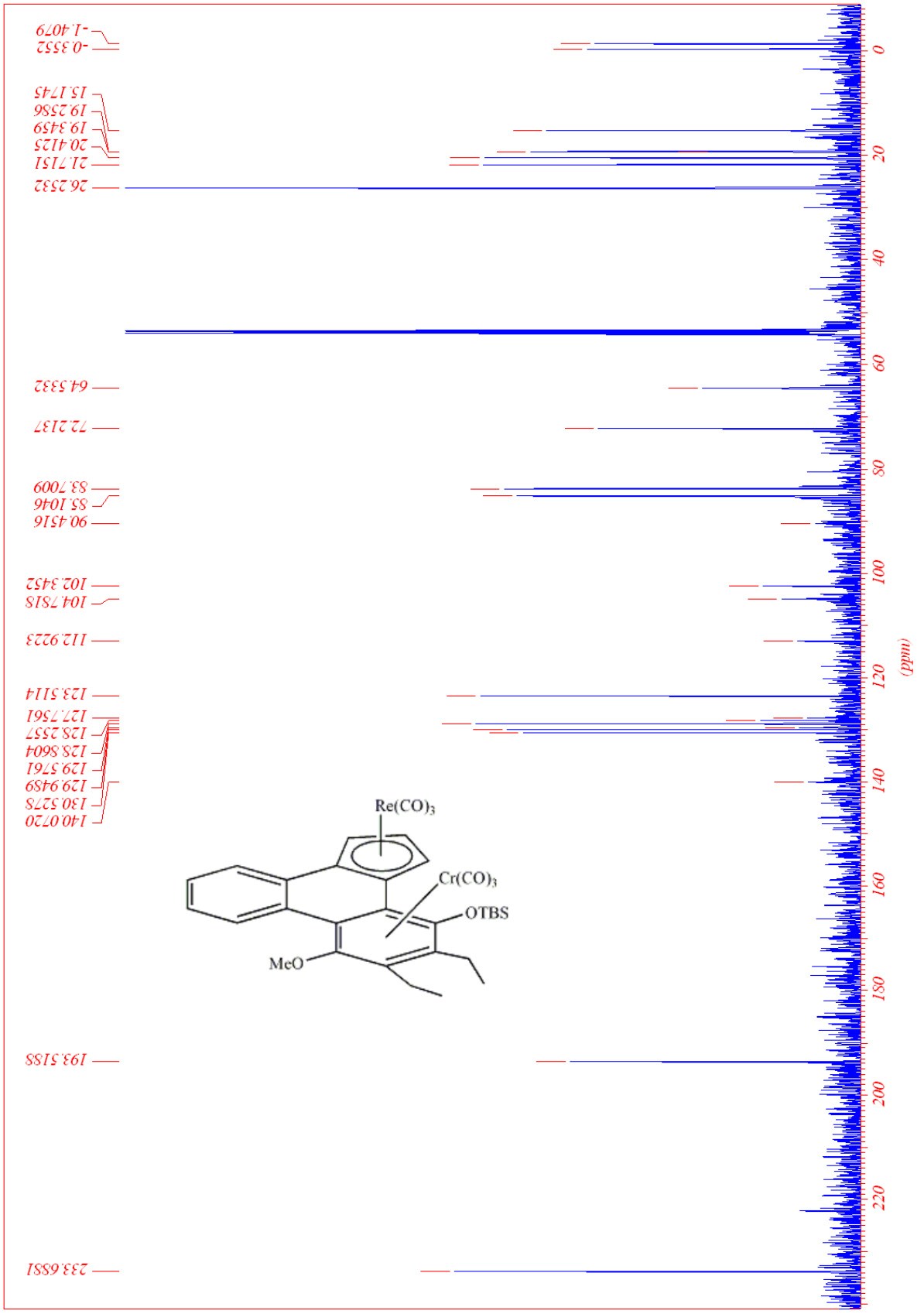
^{13}C-NMR spectrum of complex 24



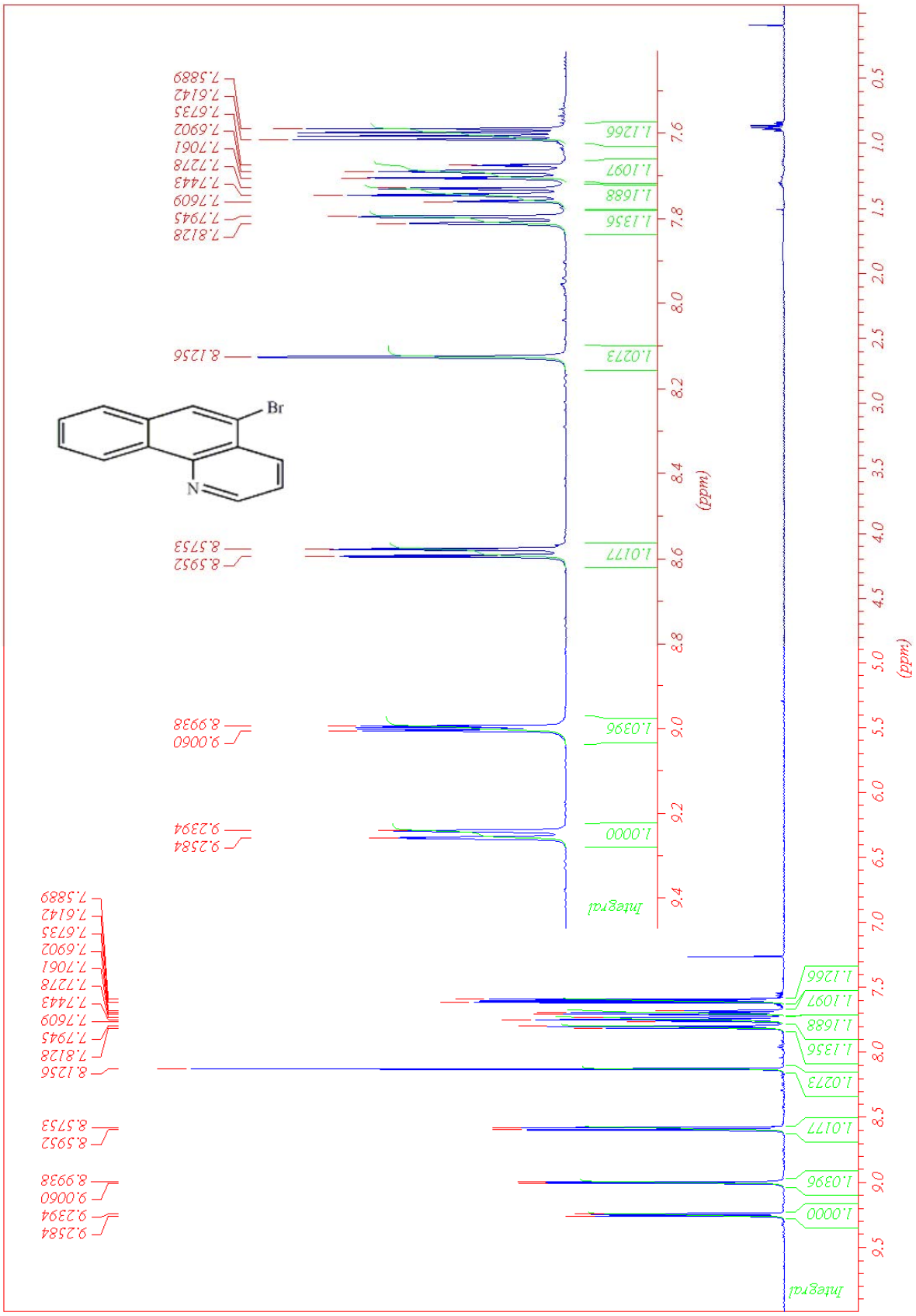
[1]H-NMR Spectrum of complex 25



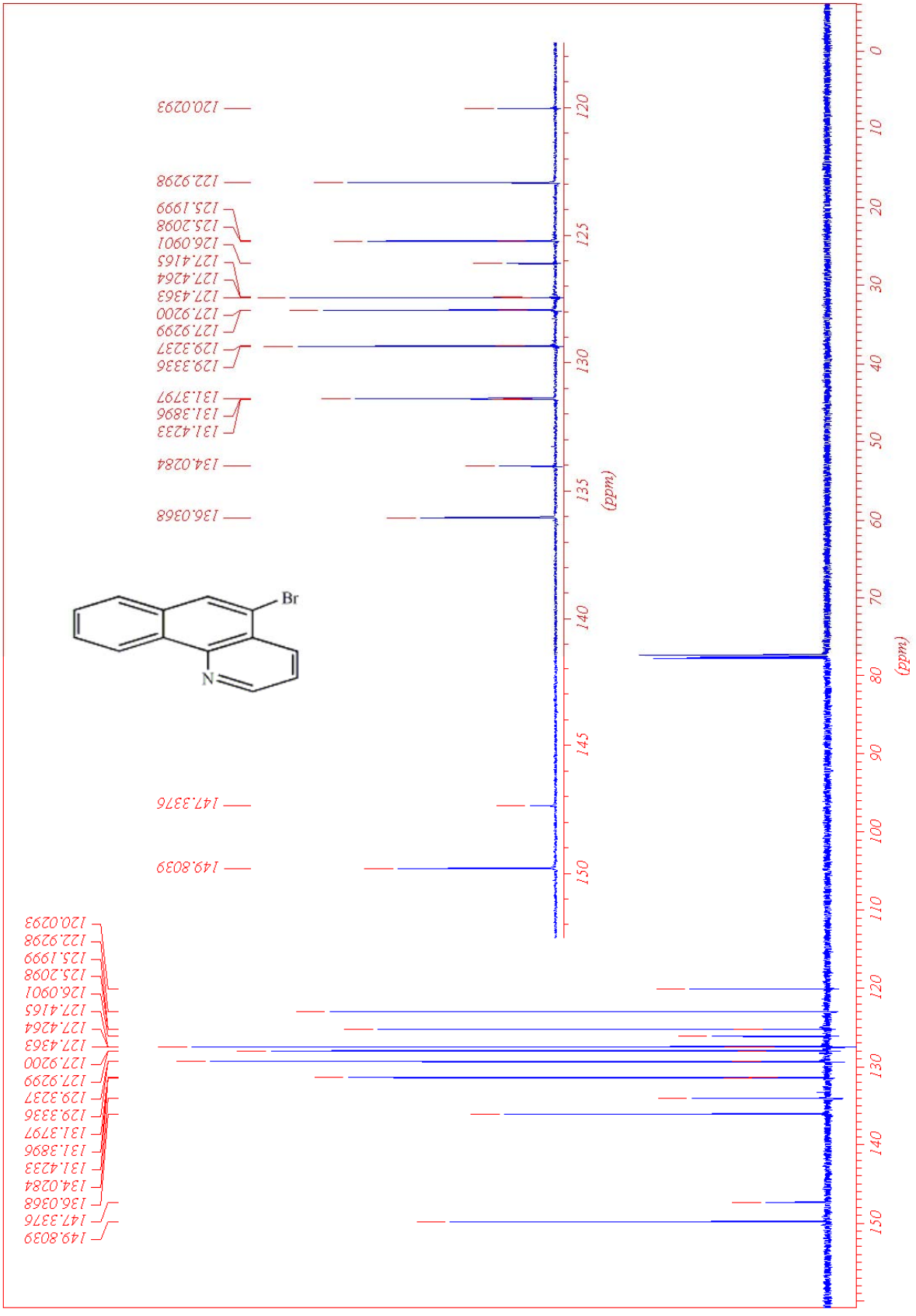
^{13}C-NMR spectrum of complex 25



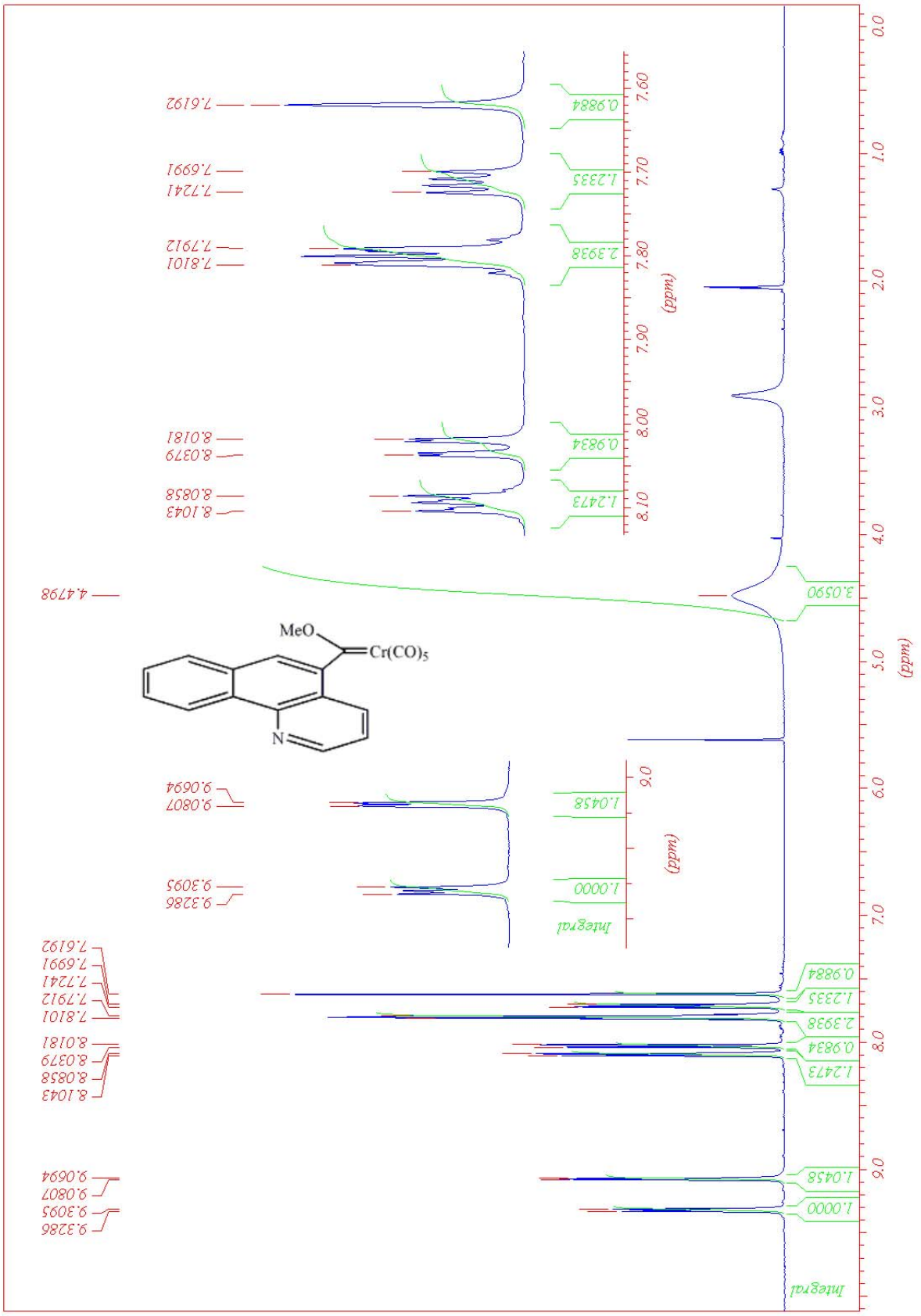
[1]H-NMR Spectrum of complex 28



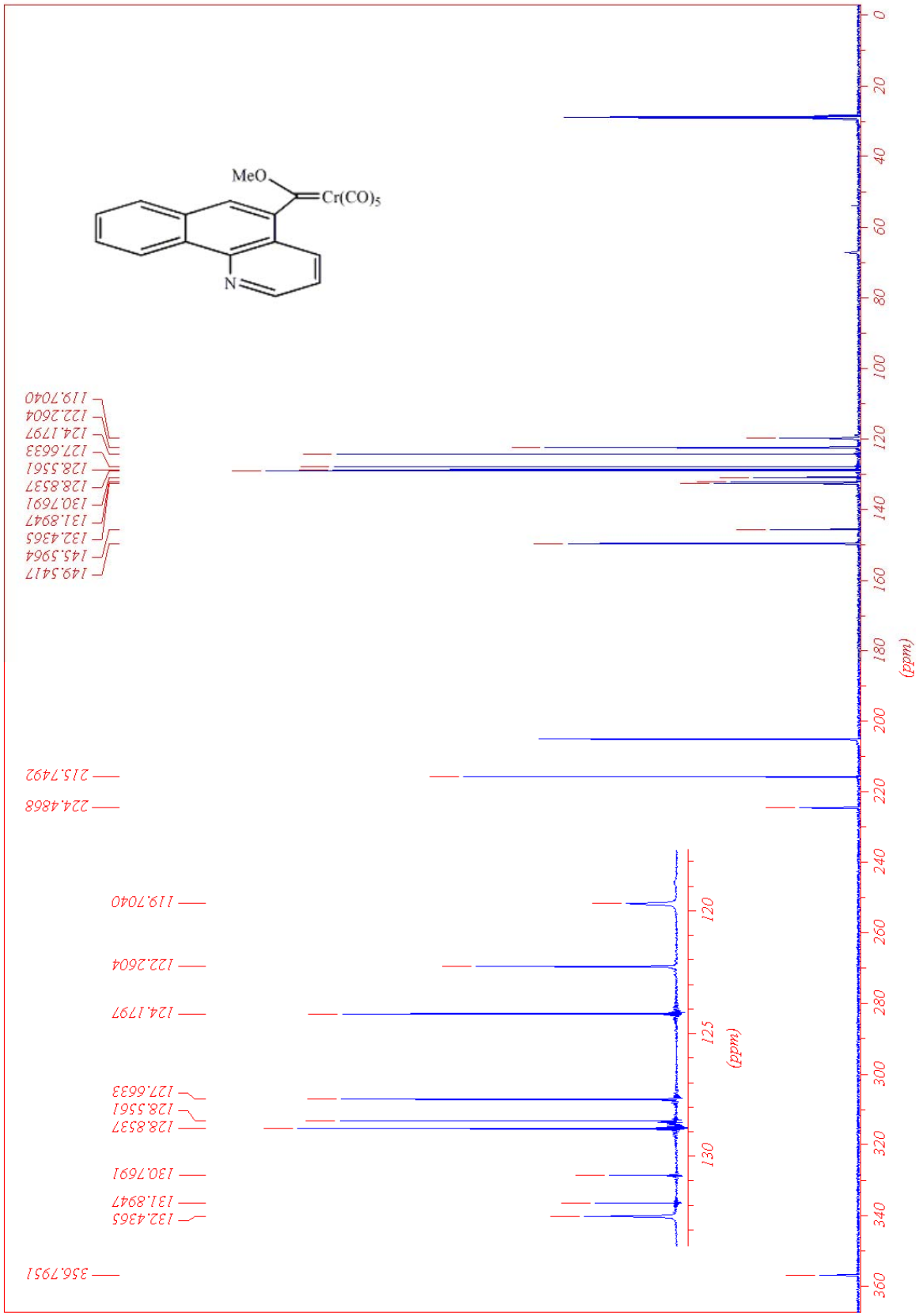
^{13}C-NMR spectrum of complex 28



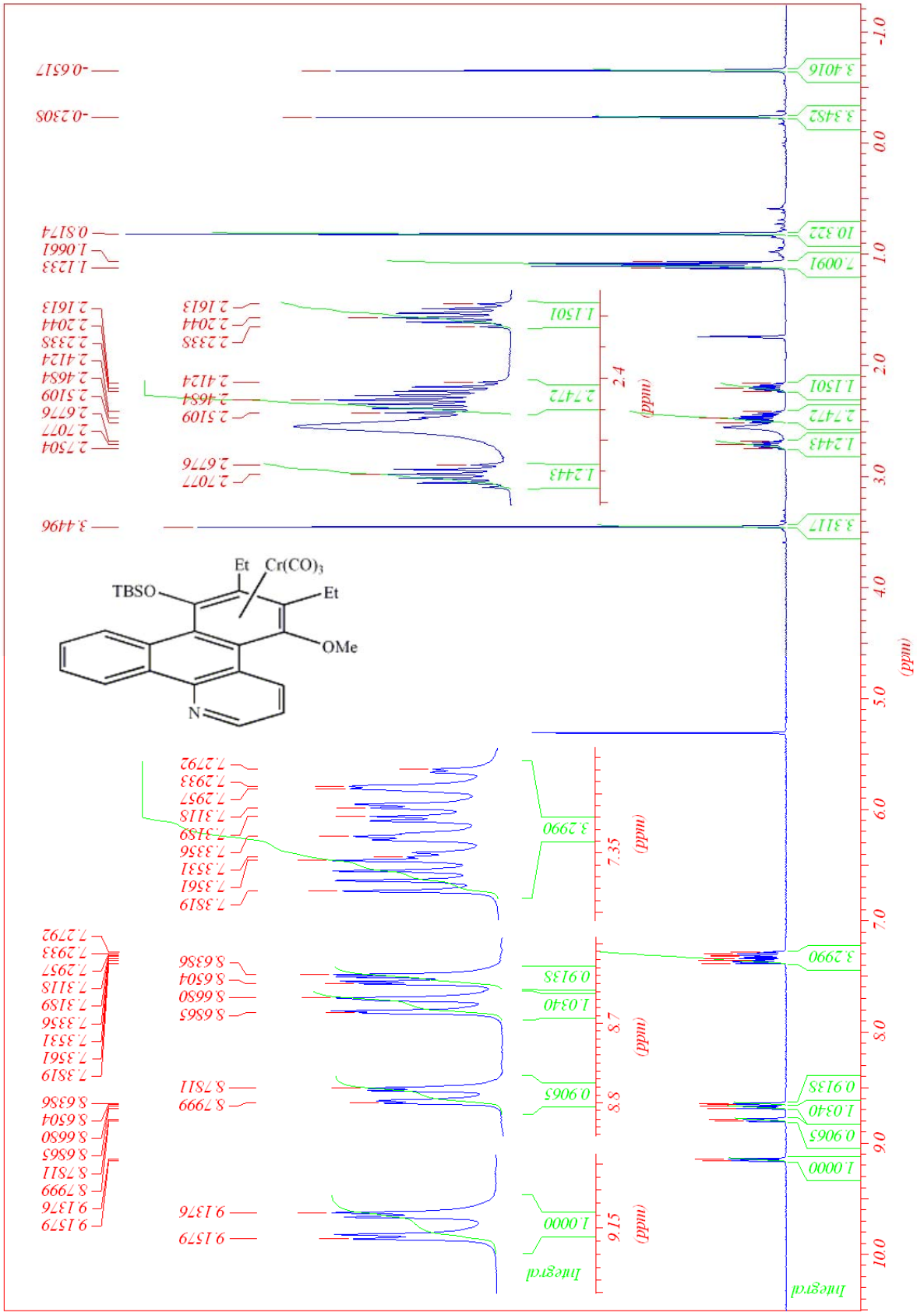
[1]H-NMR Spectrum of complex 29



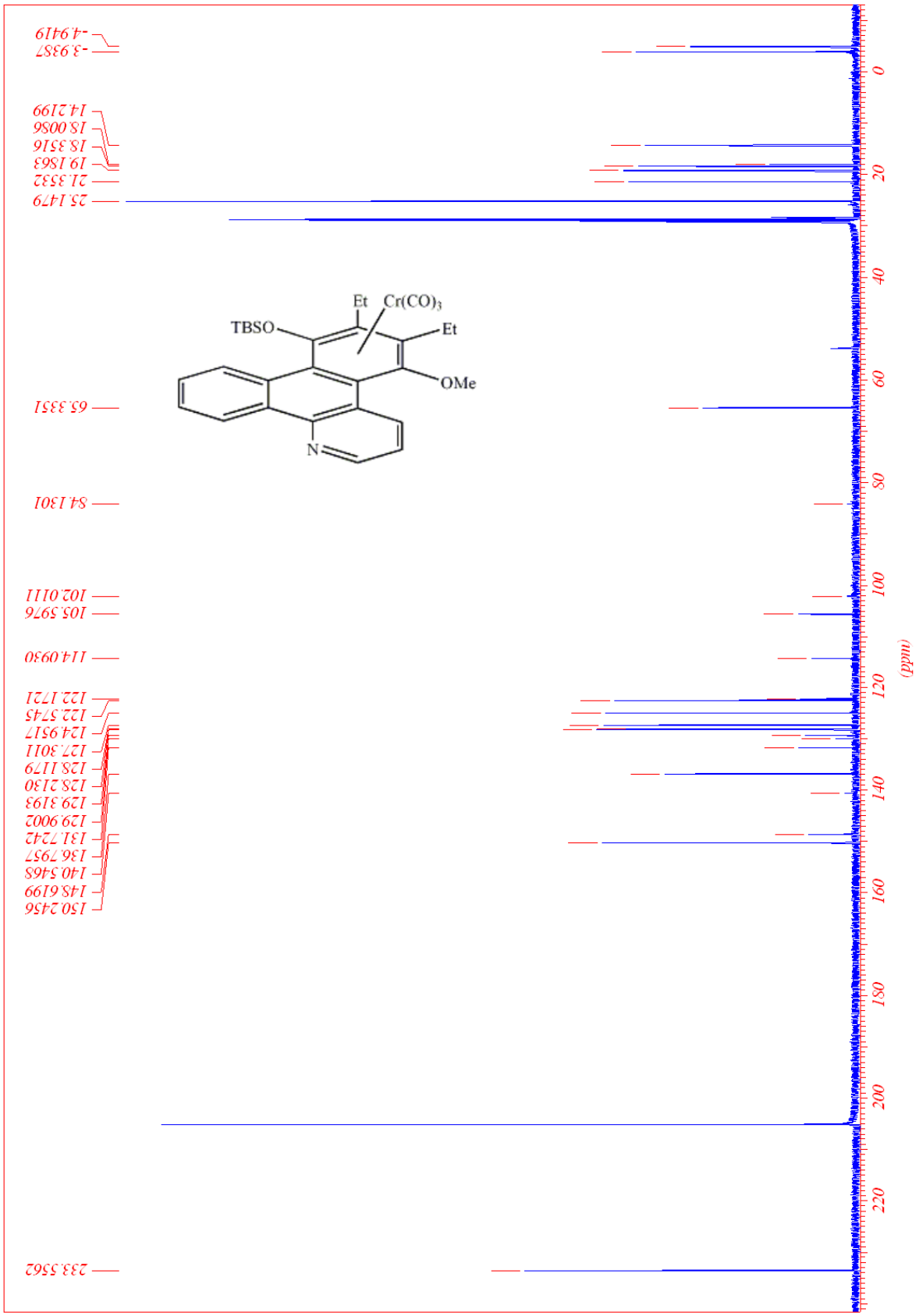
^{13}C-NMR spectrum of complex 29



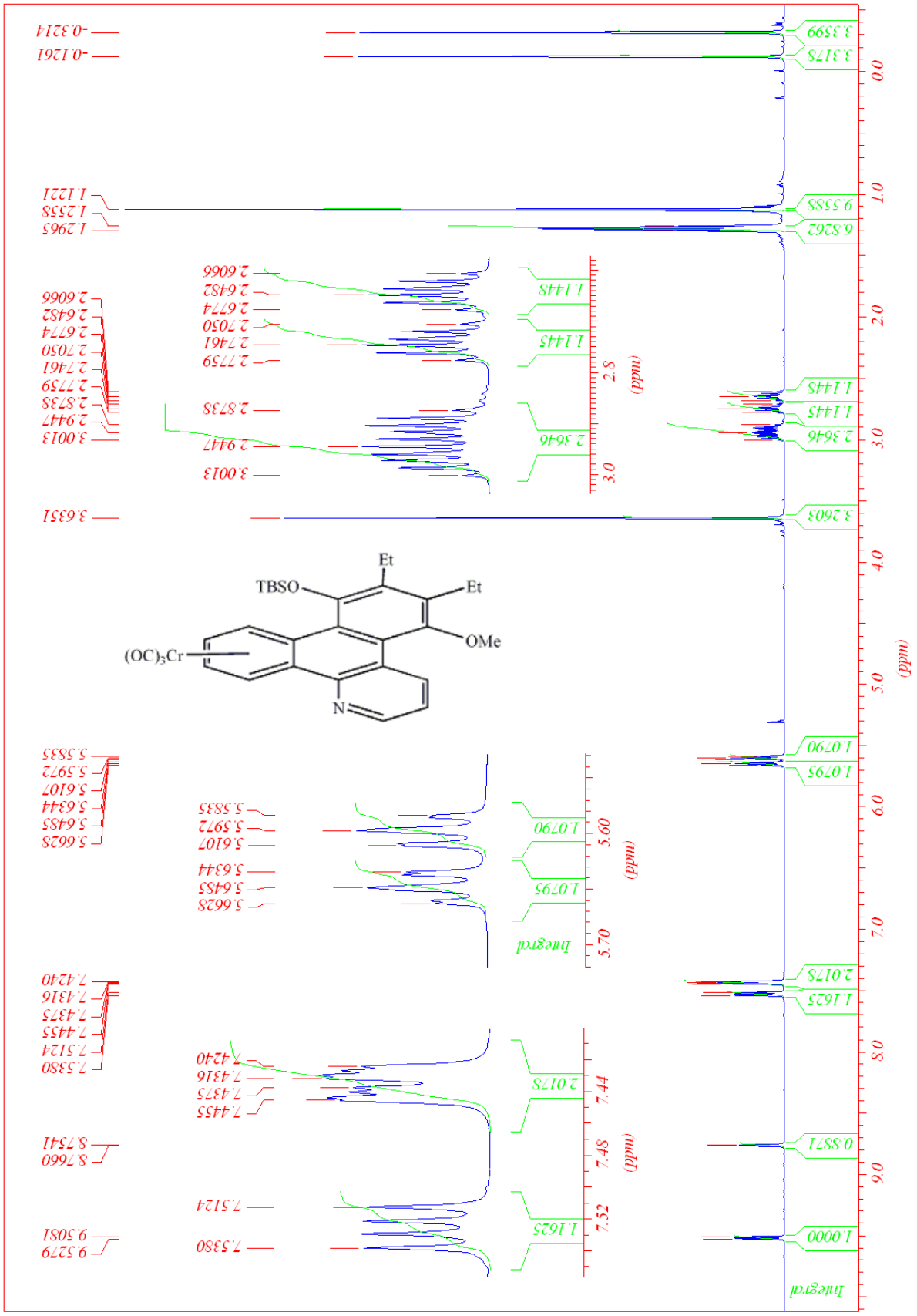
^{1}H-NMR Spectrum of complex 30



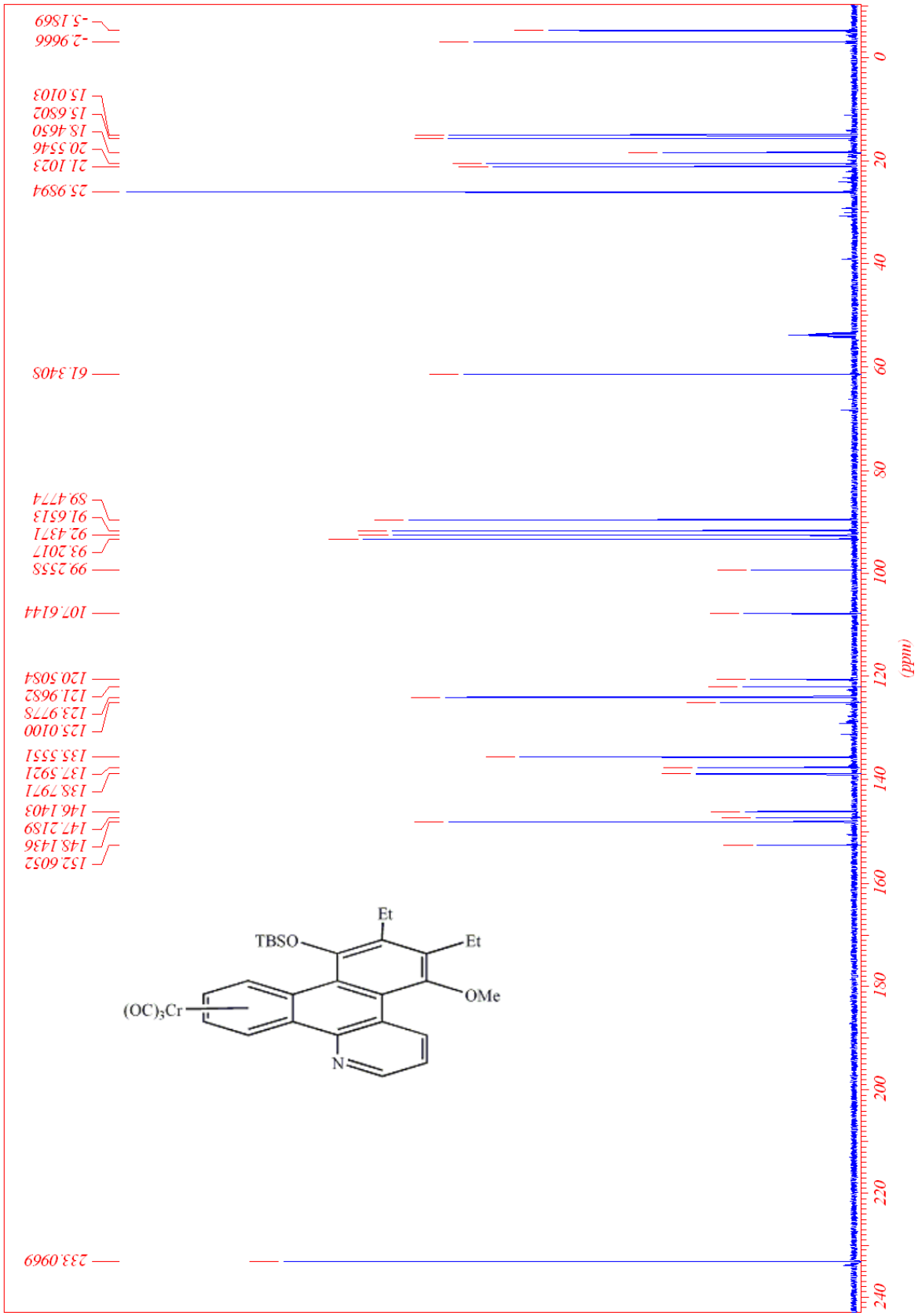
^{13}C-NMR spectrum of complex 30



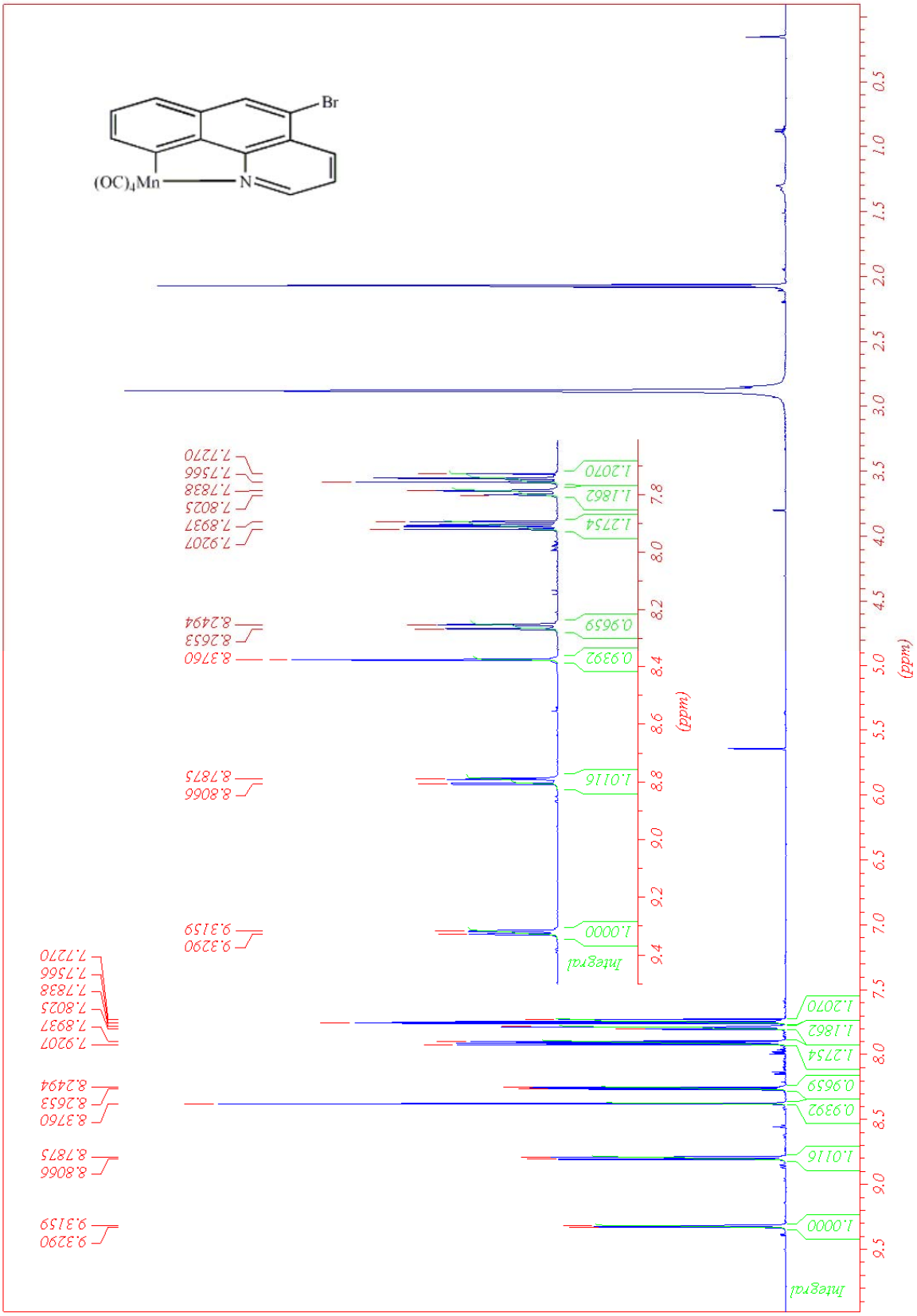
^{1}H-NMR Spectrum of complex 31



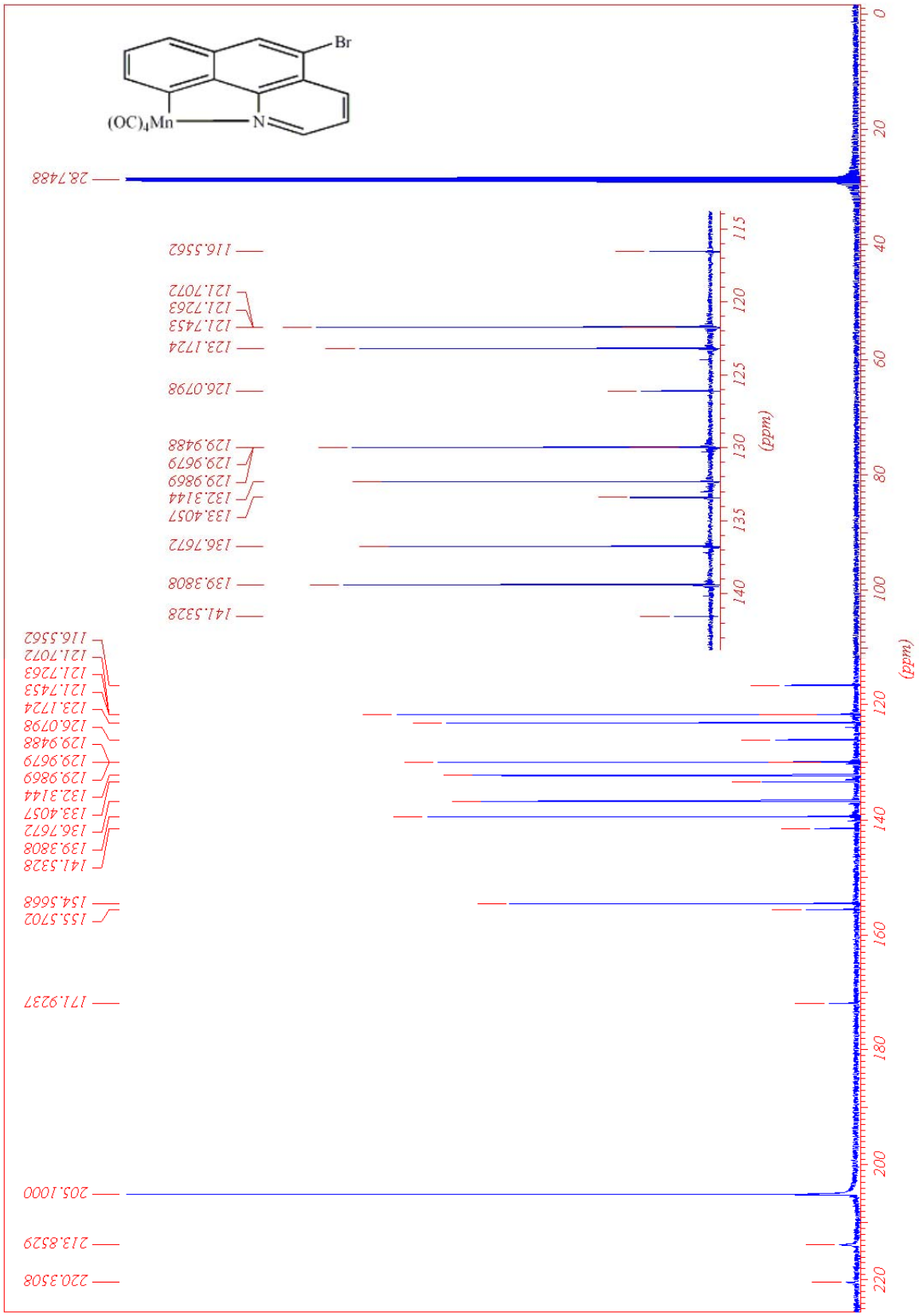
^{13}C-NMR spectrum of complex 31



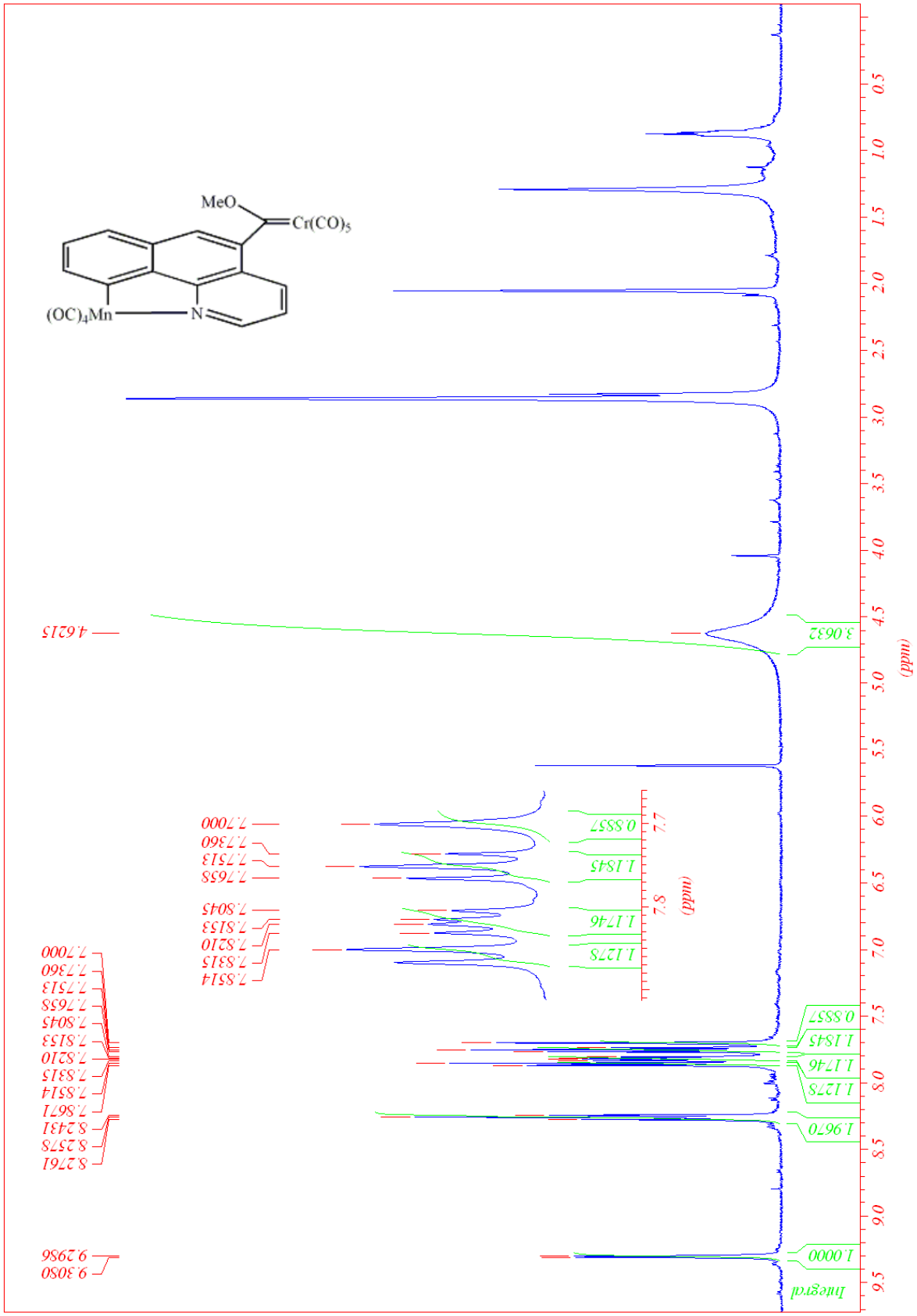
^{1}H-NMR Spectrum of complex 32



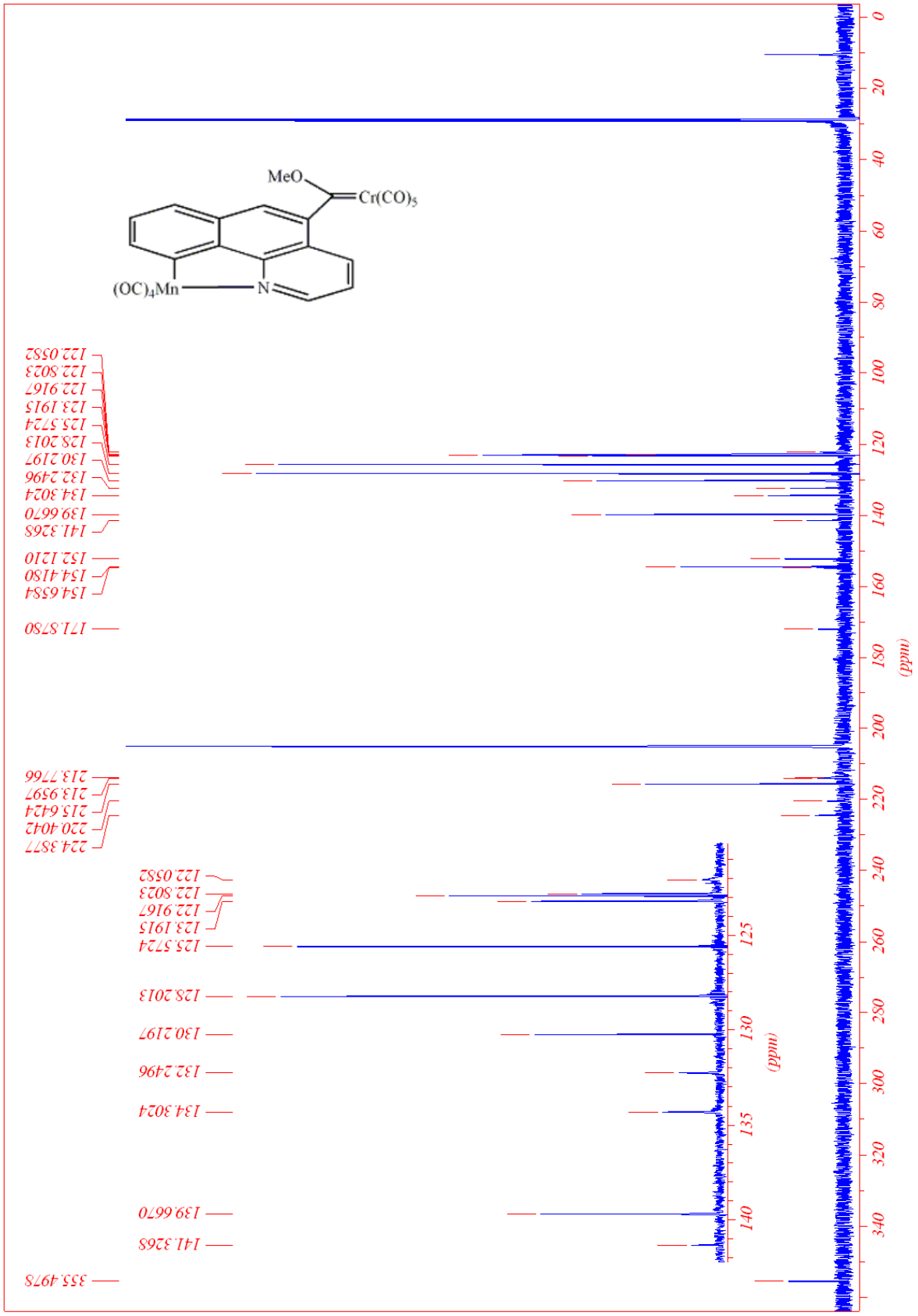
^{13}C-NMR spectrum of complex 32



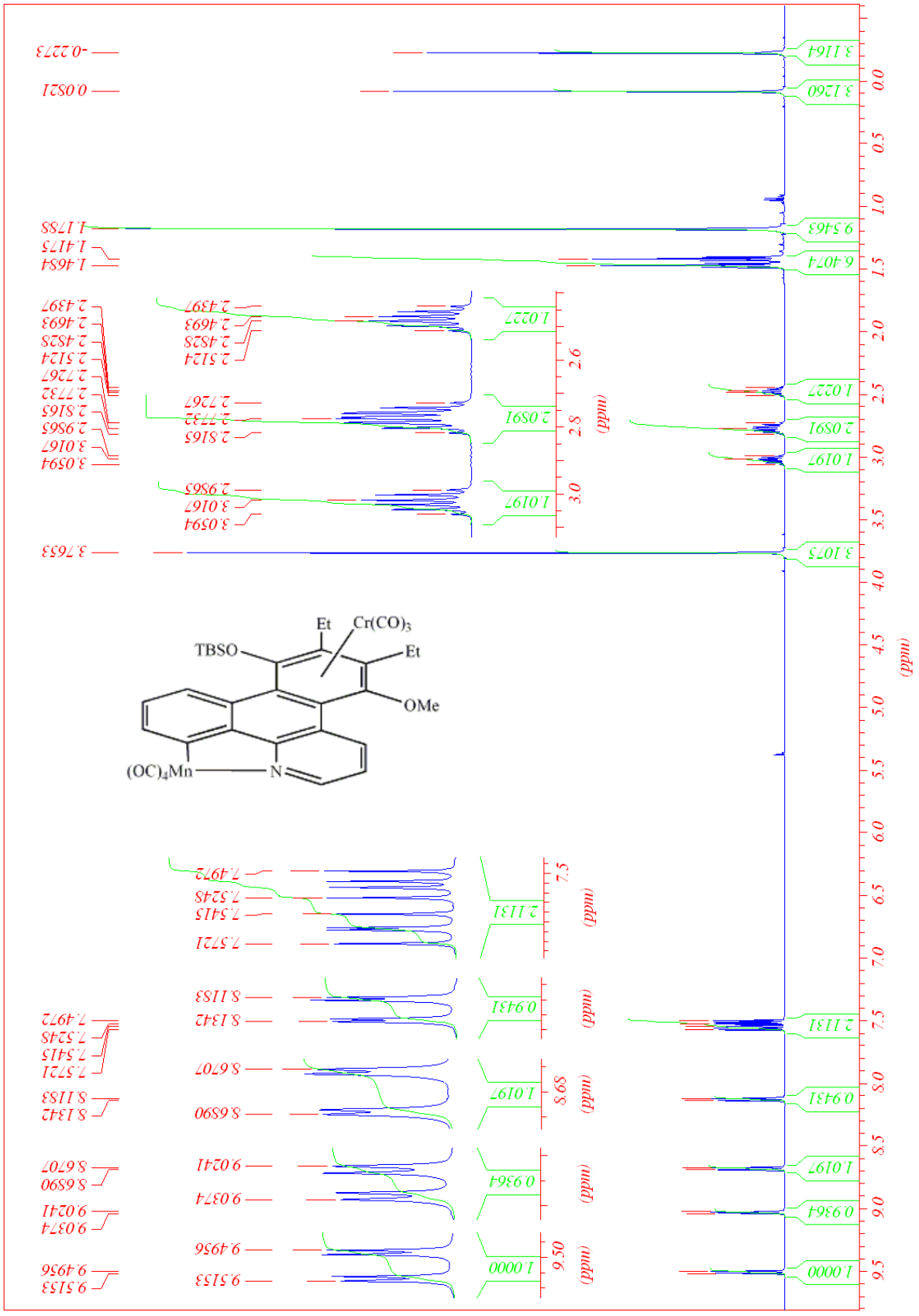
[1]H-NMR Spectrum of complex 33



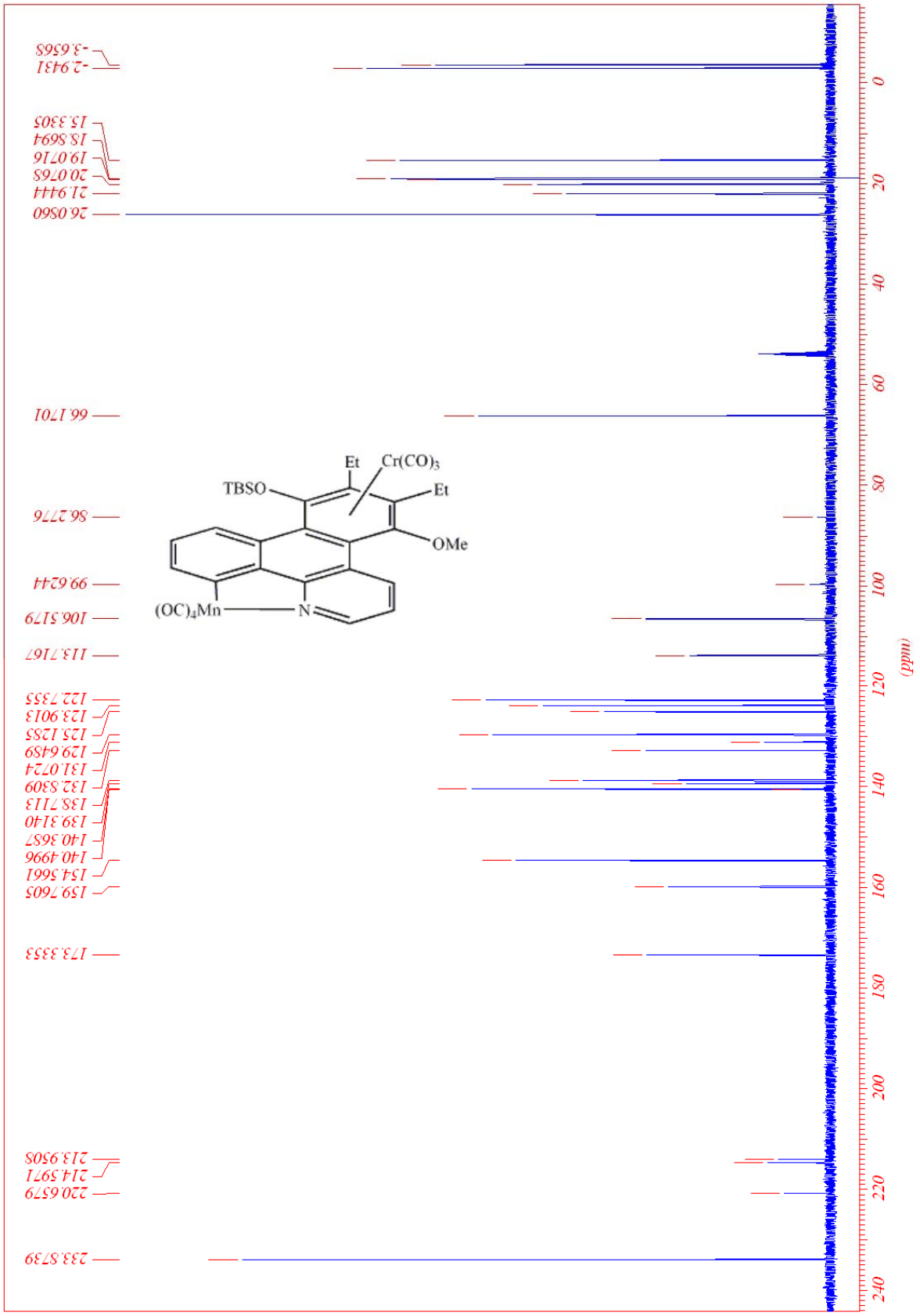
^{13}C-NMR spectrum of complex 33



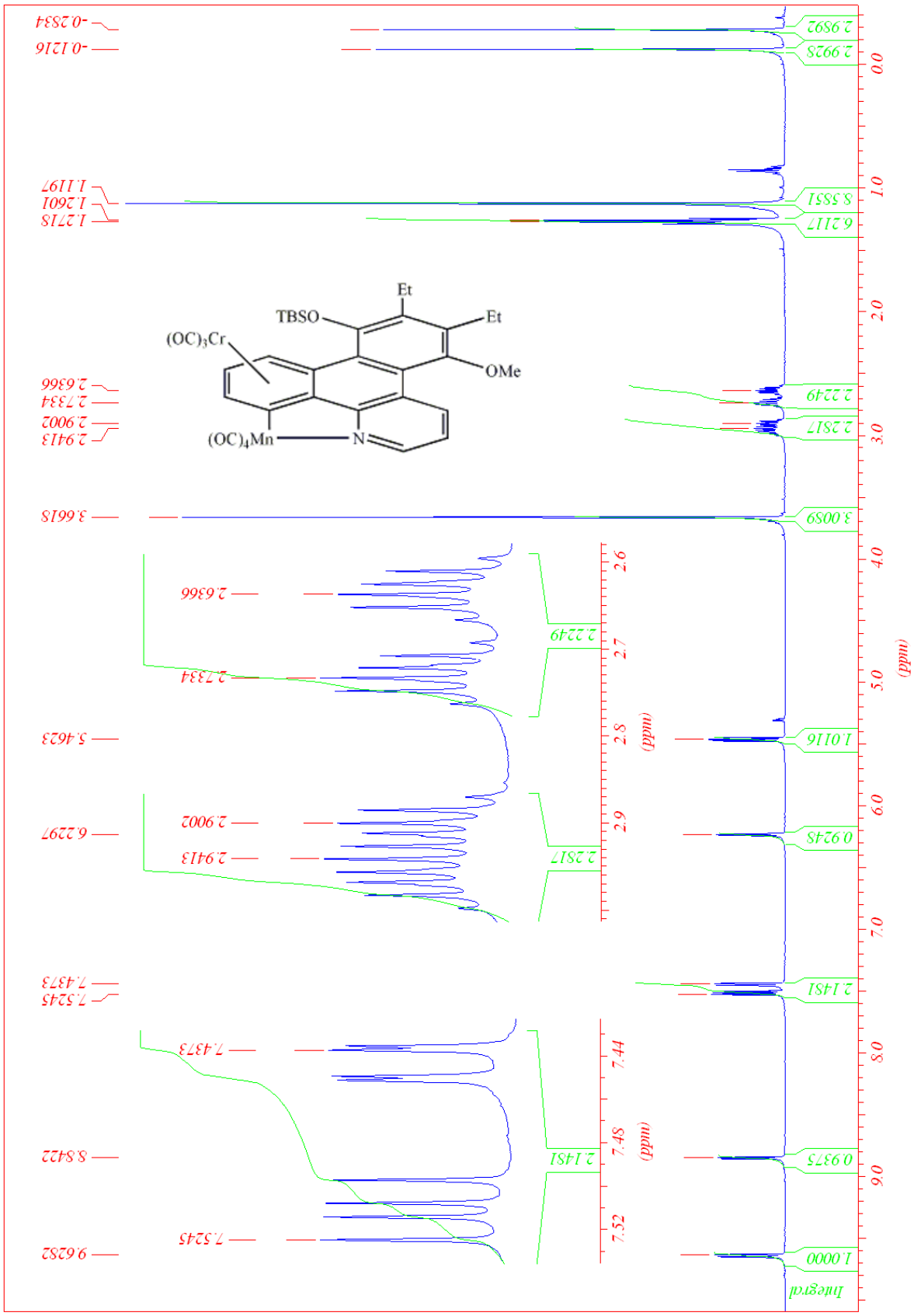
[1]H-NMR Spectrum of complex 34



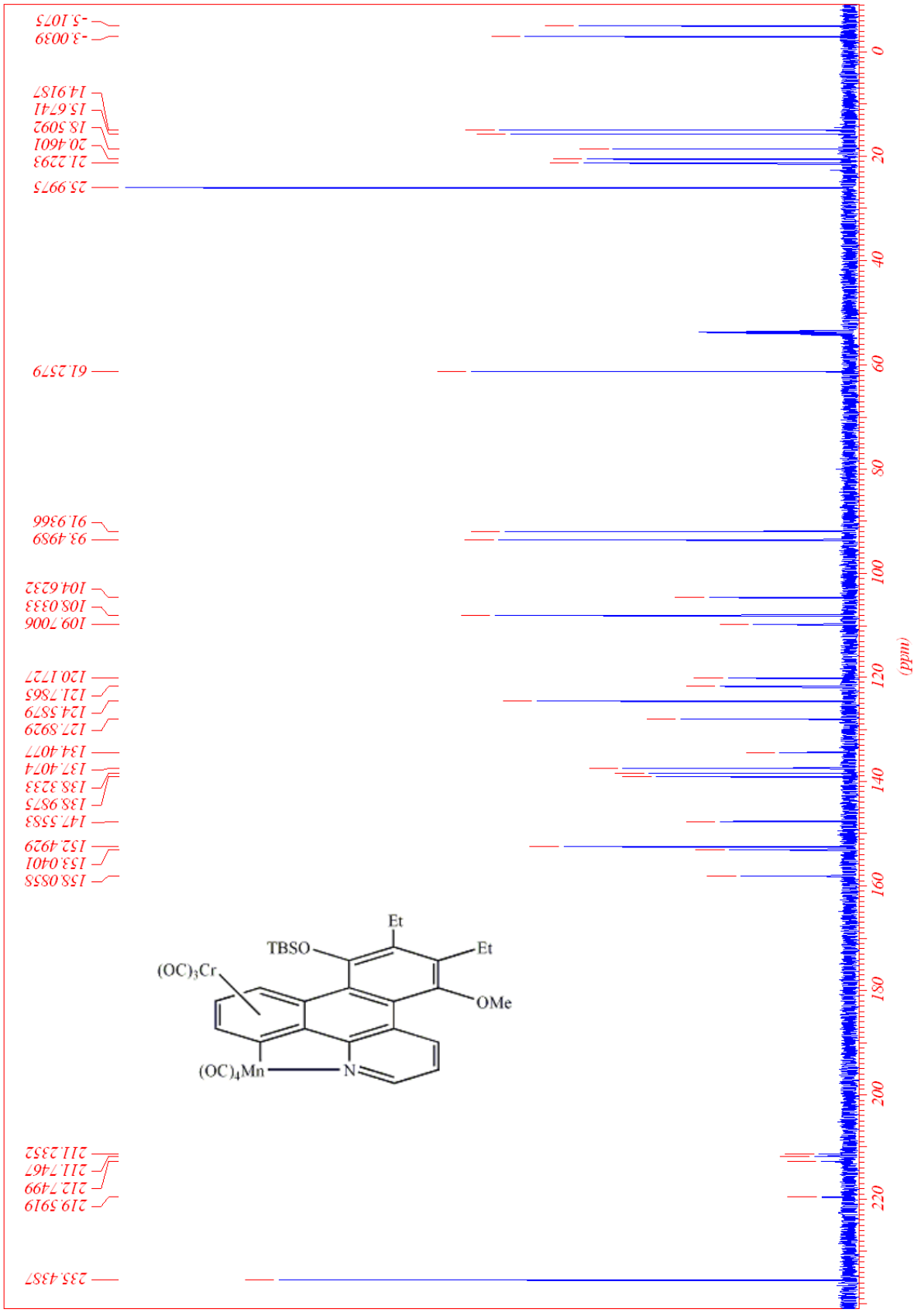
^{13}C-NMR spectrum of complex 34



[1]H-NMR Spectrum of complex 35



^{13}C-NMR spectrum of complex 35



4. Posters and publications

4.1 Posters

Templat-Tuning in Mono- und Bimetall-Phenanthren-Komplexen.
K. H. Dötz, D. Adinegara, J. Bennewitz, J. Dubarle Offner, O. Joistgen, D. Möhring, B. Santhamma, C. Steins, B. Wenzel, Doktorandenworkshop des SFB 624, November 2005, Schleiden.

Bimetallic complexes of polycyclic arenes: Synthesis and haptotropic metal migration.
J. Bennewitz, O. Joistgen, J. Dubarle Offner, J. Heil, K. H. Dötz, SFB Symposium: „Complex Molecular Architectures on Surfaces“, October 2006, Bonn.

Heterobimetallic Cr-Mn-complexes of fused arenes: Synthesis and haptotropic metal migration.
J. Dubarle Offner, R. Frölich, O. Kataeva, K. H. Dötz, 5. Ferrocentagung, February 2007, Kaiserslautern.

Controlled Haptotropic Migration of Metal Templates.
J. Bennewitz, D. Breitbach, J. Dubarle Offner, P. Hegele, O. Joistgen, K.H. Dötz, SFB Symposium, September 2007, Bonn.

Metall- und Ligand-templatgesteuerte haptotrope Metallwanderung in Aren-(Di)Metall-Komplexen.
J. Bennewitz, D. Breitbach, J. Dubarle-Offner, O. Joistgen, P. Hegele, C. Rang, M. Nieger, G. Schnakenburg, C. Schmitz, M. Sokolowski, B. Lanova, H. Baltruschat, A. Pfletschinger, M. Dolg, F. Neese, K. H. Dötz, SFB Symposium, October 2008, Bonn.

4.2 Publications

New access to a tricycle[3.2.1.$0^{2,7}$]oct-3-ene Structure.
J. Dubarle Offner, J. Marrot, M.-N. Rager, F. Le Bideau, G. Jaouen, *Synlett*, **2007**, *7*, 800.

(η^6-*N*-heterocyclic polyarene)tricarbonylchromium and cyclomanganated (η^6-*N*-heterocyclic polyarene)tricarbonylchromium complexes: Chromium-templated-[3+2+1] benzannulation and haptotropic metal migration.
J. Dubarle Offner, G. Schnakenburg, F. Rose-Munch, E. Rose, K. H. Dötz, in preparation.

Heterobimetallic Cr-Mn-complexes of fused arenes: Chromium-templated-[3+2+1] benzannulation of a cymanthrene-type metal carbene and haptotropic metal migration.
J. Dubarle Offner, R. Fröhlich, F. Rose-Munch, E. Rose, K. H. Dötz, in preparation.

Synthesis of heterobimetallic $Cr(CO)_3$-$Re(CO)_3$ complexes of oligocyclic fused arenes via a Chromium-templated-[3+2+1] benzannulation.
J. Dubarle Offner, G. Schnakenburg, F. Rose-Munch, E. Rose, K. H. Dötz, in preparation.

5. Curriculum vitae